X-Ray Crystal Structures of μ_4-Chloro-{tris[trichloro(thiosemicarbazide)-bismuth(III)]}[tris(thiosemicarbazide)bismuth(III)] Hexachlorobismuthate(III) Chloride and *catena*-μ-Chloro-dichlorobis(ethylenethiourea)-bismuth(III)

By **Luigi P. Battaglia, Anna Bonamartini Corradi, Mario Nardelli,*** and **Maria E. Vidoni Tani,** Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., 43100 Parma, Italy

The crystal structures of the title complexes (1) and (2) have been determined by three-dimensional Patterson–Fourier and least-squares methods based on *X*-ray (Mo-K_α) diffraction data. Crystal data are: (1), a = 14.056(5), c = 39.571(14) Å, Z = 9, space group $R\bar{3}$, R 0.0740; (2), a = 9.595(1), b = 17.445(2), c = 8.678(1) Å, β = 96.72(1)°, Z = 4, space group $C2/c$, R 0.049. The structure of (1) consists of an octahedral $[BiCl_6]^{3-}$ anion, a chloride ion, and a tetramer $[Bi_4Cl_{10}(tsc)_6]^{2+}$ (tsc = thiosemicarbazide), formed by an octahedral μ_3-chloro-tris-[trichloro(thiosemicarbazide)bismuthate(III)] anion and a tris(thiosemicarbazide)bismuth(III) cation, in which the co-ordination of the metal is trigonal antiprismatic. In (2) the co-ordination at bismuth is octahedral involving two ethylenethiourea molecules and four chloride ions, two of them bridging adjacent bismuth atoms forming infinite zigzag chains running along [001].

OUR previous studies on adducts of $BiCl_3$ and thiourea [1,2] showed that bismuth can form anionic and cationic complexes present in the same crystals. A similar situation is now found in the adduct (1) which thiosemicarbazide (tsc) forms with $BiCl_3$, while in the ethylenethiourea (etu) adduct (2) polymer chains of $Bi(etu)_2Cl_3$ complex molecules are formed. The crystal structures of these complexes are now described.

EXPERIMENTAL

The title complexes were prepared by mixing ethanolic solutions of the reactants in the molar ratio $BiCl_3$: tsc(etu) = 1 : 2; (1) crystallizes as pale yellow thin tabular platelets, (2) gives yellow prisms. Both complexes decompose between 120 and 140 °C without melting [Found: C, 3.6; H, 1.5; Bi, 46.8; N, 12.5. Calc. for (1): C, 3.7; H, 1.5; Bi, 47.8; N, 12.8. Found: C, 14.1; H, 3.0; Bi, 40.9; N, 10.9. Calc. for (2): C, 13.9; H, 2.3; Bi, 40.2; N, 10.8%].

Crystal Data.—Complex (1), $C_4H_{20}Bi_3Cl_9N_{12}S_4$, M = 1 310.7, Trigonal, a = 14.056(5), c = 39.571(14) Å, U = 6 771(5) Å^3, D_m = 2.86 g cm^{-3}, Z = 9, D_c = 2.88 g cm^{-3}, $F(000)$ = 5 346, Mo-K_α radiation (λ 0.710 69 Å), μ(Mo-K_α) = 185.5 cm^{-1}, space group $R\bar{3}$.

Complex (2), $C_6H_{12}BiCl_3N_4S_2$, M = 519.8, Monoclinic, a = 9.595(1), b = 17.445(2), c = 8.678(1) Å, β = 96.72(1)°, U = 1 442.6(3) Å^3, D_m = 2.38 g cm^{-3}, Z = 4, D_c = 2.39 g cm^{-3}, $F(000)$ = 968, Mo-K_α radiation (λ 0.710 69 Å), μ(Mo-K_α) = 130.1 cm^{-1}, space group $C2/c$.

For both complexes, cell dimensions were determined first from rotation and Weissenberg photographs (Cu-K_α) and then refined by diffractometer measurements (Mo-K_α).

Intensity-data Collection.—A crystal of (1) (0.05 × 0.24 × 0.38 mm) was aligned with the axis coincident with [010] on an automated Siemens AED single-crystal diffractometer. 6 774 Reflections were collected using the ω—2θ scan technique in the interval $6 < 2\theta < 50°$; of these, 3 023 having $I < 3\sigma(I)$ were considered 'unobserved'. The remaining 3 751 were used in the analysis after correction for Lorentz and polarization effects. The intensities of symmetry-equivalent reflections were averaged to give 1 551 unique observations. For (2), 1 602 reflections were collected in the range $6 < 2\theta < 54°$ by the same technique for a crystal of dimensions 0.09 × 0.19 × 0.61 mm; of these, 1 391 for which $I < 2\sigma(I)$ were used in the crystal analysis after the usual data reduction. During data collection a standard reflection was measured every 20 reflections and its intensity was found to be constant in both cases. No correction for absorption was made. The absolute scale was obtained first by the Wilson method, then as a least-squares parameter.

Structure Analysis.—For both structures the bismuth atoms were located from three-dimensional Patterson maps and the positions of the other non-hydrogen atoms were determined by the heavy-atom technique. For (1), full-matrix least-squares refinement of all the positional and thermal parameters (anisotropic for Bi, Cl, and S and isotropic for N and C, since anisotropic refinement of nitrogen and carbon did not improve the agreement between the

---

[1] L. P. Battaglia, A. Bonamartini Corradi, G. Pelizzi, and M. E. Vidoni Tani, *Cryst. Struct. Comm.*, 1975, **4**, 399.

[2] L. P. Battaglia, A. Bonamartini Corradi, G. Pelizzi, and M. E. Vidoni Tani, *J.C.S. Dalton*, 1977, 1141.

observed and calculated structure factors) minimizing the function $\Sigma w|\Delta F|^2$ with unit weights converged to R 0.074. Three reflections, (009), (0 0 15), and (0 0 18), considered to be affected by extinction were excluded from the refinement. Refinement for (2) was by block-diagonal least squares with anisotropic thermal parameters down to R 0.049. No attempts were made to locate the hydrogen atoms in either structure. Table 1 shows positional parameters for (1) and (2) respectively. The atomic scattering factors used were those of Cromer and Mann.[3] All the calculations were performed on the Cyber 7600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Bologna using the SHELX system [4] for (1) and programs written by Immirzi [5] for (2). Observed and calculated structure factors with thermal parameters are available as Supplementary Publication No. SUP 22216 (20 pp.).*

TABLE 1

Final fractional co-ordinates (× 10^4 for Bi, Cl, and S; × 10^3 for N and C) with estimated standard deviations in parentheses

	x/a	y/b	z/c
(*a*) For (1)			
Bi(1)	−303(1)	1 743(1)	−2 305(1)
Bi(2)	0	0	−3 405(1)
Bi(3)	0	0	0
Cl(1)	0	0	−2 617(5)
Cl(2)	−314(10)	2 138(9)	−2 950(4)
Cl(3)	−2 343(9)	5(9)	−2 318(4)
Cl(4)	63(9)	1 784(11)	−1 624(4)
Cl(5)	1 766(9)	544(9)	377(4)
Cl(6)	0	0	5 000
S(1)	−1 417(9)	2 737(9)	−2 209(4)
S(2)	26(9)	1 436(9)	−3 841(3)
N(1)	111(3)	375(3)	−221(1)
N(2)	60(3)	440(3)	−208(1)
N(3)	−77(3)	471(3)	−199(1)
N(4)	179(3)	200(3)	−330(1)
N(5)	184(3)	287(3)	−351(1)
N(6)	115(4)	356(4)	−388(1)
C(1)	−40(4)	403(4)	−208(1)
C(2)	107(4)	268(4)	−372(1)
(*b*) For (2)			
Bi	0	1 067(1)	2 500
Cl(1)	0	0	0
Cl(2)	2 832(4)	1 145(3)	2 916(5)
S	−19(4)	2 122(2)	212(5)
N(1)	51(2)	361(1)	50(2)
N(2)	203(1)	292(1)	201(2)
C(1)	90(2)	291(1)	96(2)
C(2)	154(2)	420(1)	117(2)
C(3)	252(2)	371(1)	234(2)

DISCUSSION

$3BiCl_3\cdot4tsc$, (1).—The structure of $3BiCl_3\cdot4tsc$ consists of a $[Bi_4Cl_{10}(tsc)_6]^{2+}$ cation and a chloride ion both on the same three-fold axis, and an octahedral $[BiCl_6]^{3-}$ anion at 0,0,0 on a $\bar{3}$ axis (Figure 1). The cation is a tetramer formed by one chloride ion tetrahedrally surrounded by four bismuth atoms, three of which are symmetry related by the three-fold axis and the fourth lies on that axis. The Bi(2)–Cl(1) bond (Table 2) is significantly longer than the other Bi–Cl bonds, so the tetrahedron is elongated along the three-fold axis and the $[Bi_4Cl_{10}(tsc)_6]^{2+}$ cation can be considered as formed by the interaction between a tris(thiosemicarbazide)bismuth(III) cation and a μ_3-chloro-tris[trichloro(thiosemicarbazide)-bismuthate(III)] anion. In the anion the bismuth co-ordination is distorted octahedral and involves four chlorine atoms and one thiosemicarbazide molecule forming a five-membered chelate ring *via* sulphur and the hydrazinic terminal nitrogen. The distortion of the octahedron surrounding Bi(1) is indicated by the values of the angles involving the *cis* atoms which range from 74.2 to 128.7° [the largest displacement from the theoretical value is shown by N(1)–Bi(1)–Cl(1)] and by the values of the angles involving the *trans* atoms (Table 2). A long contact (3.40 Å) between Bi(1) and a Cl(3) ion belonging to an adjacent polyhedron complete

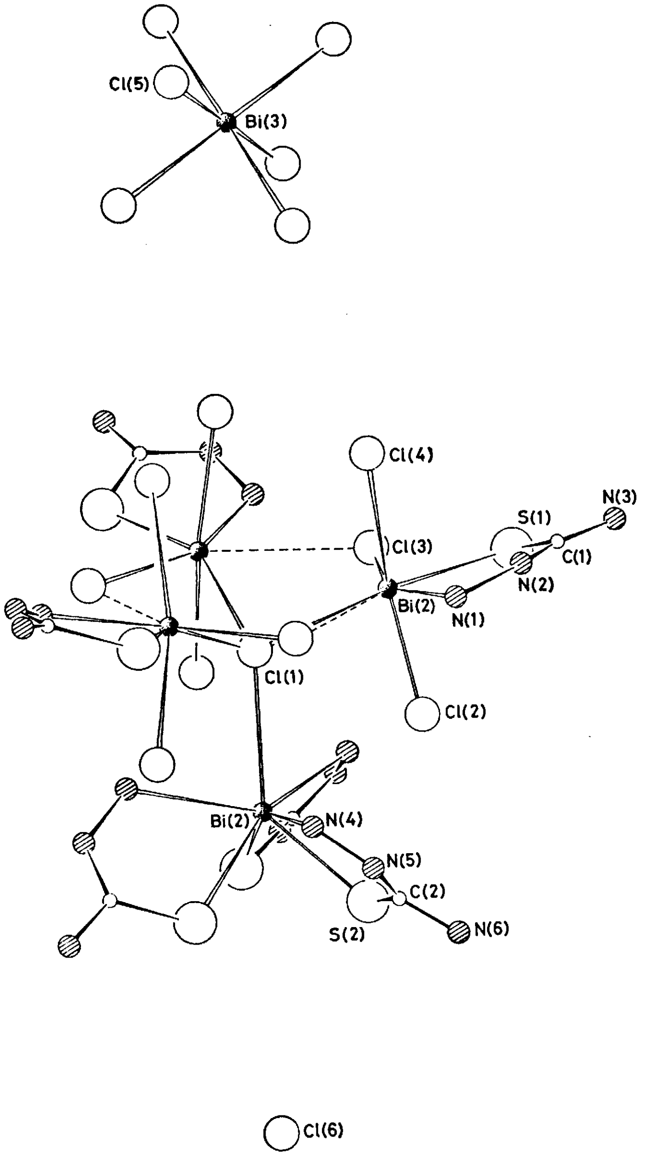

FIGURE 1 Clinographic projection of complex (1)

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[3] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[4] G. Sheldrick, 'SHELX System of Computing Programs,' University of Cambridge, 1976.

[5] A. Immirzi, *Ricerca Sci.*, 1967, **37**, 743.

the co-ordination to give a distorted pentagonal bipyramid. In the tris(thiosemicarbazide)bismuth(III) cation the sulphur and the nitrogen atoms from the three co-ordinated thiosemicarbazide molecules are at the vertices of a trigonal antiprism, Bi(2) being 0.44 Å below the plane determined by the N(4) atoms. The central bridging Cl(1) ion occupies a seventh co-ordination site along the line passing through the centre of the basal face determined by the sulphur atoms, so that the co-ordination polyhedron of Bi(2) can be considered as a monocapped trigonal antiprism.

TABLE 2

Bond distances (Å) and angles (°) in (1) with estimated standard deviations in parentheses

Bi(1)–Cl(1)	2.96(1)	Bi(3)–Cl(5)	2.66(1)
Bi(1)–Cl(2)	2.61(2)	S(1)–C(1)	1.74(5)
Bi(1)–Cl(3)	2.68(1)	C(1)–N(3)	1.35(7)
Bi(1)–Cl(4)	2.74(2)	C(1)–N(2)	1.23(6)
Bi(1)–S(1)	2.60(1)	N(2)–N(1)	1.50(6)
Bi(1)–N(1)	2.54(4)	S(2)–C(2)	1.70(5)
Bi(2)–Cl(1)	3.12(2)	C(2)–N(5)	1.27(6)
Bi(2)–S(2)	2.64(1)	C(2)–N(6)	1.35(8)
Bi(2)–N(4)	2.71(4)	N(4)–N(5)	1.46(9)
Cl(1)–Bi(1)–N(1)	128.7(9)	S(1)–Bi(1)–Cl(3)	80.5(4)
Cl(1)–Bi(1)–Cl(2)	77.7(5)	S(1)–Bi(1)–Cl(4)	90.1(5)
Cl(1)–Bi(1)–Cl(3)	76.6(3)	Cl(3)–Bi(1)–Cl(4)	98.2(4)
Cl(1)–Bi(1)–Cl(4)	109.0(5)	S(2)–Bi(2)–N(4)	70.2(9)
Cl(2)–Bi(1)–N(1)	89.4(9)	N(4)–Bi(2)–N(4^{i}) *	117(1)
Cl(2)–Bi(1)–S(1)	87.7(5)	S(2)–Bi(2)–S(2^{i})	82.0(4)
Cl(2)–Bi(1)–Cl(3)	93.3(4)	N(4)–Bi(2)–Cl(1)	80.8(8)
N(1)–Bi(1)–S(1)	74.2(9)	S(2)–Bi(2)–Cl(1)	130.8(3)
N(1)–Bi(1)–Cl(4)	78.4(9)	Cl(5)–Bi(3)–Cl(5^{i})	91.6(4)
Bi(1)–S(1)–C(1)	102(2)	Bi(2)–S(2)–C(2)	106(2)
S(1)–C(1)–N(2)	127(5)	S(2)–C(2)–N(5)	127(6)
S(1)–C(1)–N(3)	115(3)	S(2)–C(2)–N(6)	116(3)
N(2)–C(1)–N(3)	118(5)	N(5)–C(2)–N(6)	117(6)
C(1)–N(2)–N(1)	123(5)	C(2)–N(5)–N(4)	121(6)
N(2)–N(1)–Bi(1)	112(2)	N(5)–N(4)–Bi(2)	114(3)

* $i = \bar{y}, x - y, z$.

The environment of Bi(3) which forms the $[BiCl_6]^{3-}$ anion is a nearly regular octahedron with a three-fold axis and a symmetry centre, indicating that the lone pair on the metal atom has no stereochemical influence. The Bi-Cl distances involving the bridging chloride ions are significantly longer than the others, as observed in other polynuclear bismuth complexes such as $BiCl_3$·7tu (tu = thiourea) [1] where a binuclear cation with two bridging chloride ions is present. The Bi–N distances are also not all equal, that in $[BiCl_3(\mu\text{-}Cl)(tsc)]^-$ being shorter than that in $[Bi(tsc)_3]^{3+}$, which corresponds to a weak interaction; the differences can be attributed to the relevant steric hindrance the ligands exert in $[Bi(tsc)_3]^{3+}$. Bond distances and angles in the two crystallographically independent thiosemicarbazide molecules are in good agreement with those found in other thiosemicarbazide complexes,[6-11] in uncomplexed thiosemicarbazide,[12,13] and in thiosemicarbazide hydrochloride,[14] the thiourea moieties being planar within experimental error. Packing in the structure is determined by N · · · Cl contacts (Table 3) some of which can be interpreted as hydrogen bonds.

TABLE 3

Contacts less than 3.50 Å for (1)

N(1) · · · Cl(4$^{\text{I}}$)	3.30(4)	N(5) · · · Cl(5$^{\text{VI}}$)	3.40(9)
N(1) · · · Cl(5$^{\text{II}}$)	3.32(4)	N(5) · · · Cl(5$^{\text{V}}$)	3.47(8)
N(2) · · · Cl(4$^{\text{III}}$)	3.21(4)	N(5) · · · Cl(2$^{\text{VI}}$)	3.34(9)
N(3) · · · Cl(4$^{\text{III}}$)	3.31(5)	N(6) · · · Cl(3$^{\text{VII}}$)	3.41(5)
N(3) · · · Cl(6$^{\text{IV}}$)	3.37(4)	N(6) · · · Cl(5$^{\text{I}}$)	3.41(6)
N(4) · · · Cl(2$^{\text{V}}$)	3.40(4)	N(6) · · · Cl(5$^{\text{V}}$)	3.47(6)

Roman numeral superscripts denote the following equivalent positions:

I $\frac{1}{3} - x, \frac{2}{3} - y, -\frac{1}{3} - z$
II $\frac{1}{3} - x + y, \frac{2}{3} - x, -\frac{1}{3} + z$
III $\frac{1}{3} + x - y, \frac{2}{3} + x, -\frac{1}{3} - z$
IV $-\frac{1}{3} - y, \frac{1}{3} + x - y, -\frac{2}{3} + z$
V $\frac{1}{3} + y, \frac{2}{3} - x + y, -\frac{1}{3} - z$
VI $\frac{2}{3} + x - y, \frac{1}{3} + x, -\frac{2}{3} - z$
VII $-\frac{1}{3} - x, \frac{1}{3} - y, -\frac{2}{3} - z$

TABLE 4

Bond distances (Å) and angles (°) in (2) with estimated standard deviations in parentheses

Bi–Cl(1)	2.859(2)	C(1)–N(2)	1.33(2)
Bi–Cl(2)	2.703(4)	N(1)–C(2)	1.50(2)
Bi–S	2.706(5)	N(2)–C(3)	1.48(2)
S–C(1)	1.72(1)	C(2)–C(3)	1.56(3)
C(1)–N(1)	1.32(2)		
Cl(1)–Bi-Cl(1^{i}) *	98.7(1)	S–Bi–S^{i}	94.3(1)
Cl(1)–Bi–Cl(2)	92.6(1)	Bi–S–C(1)	108.0(6)
Cl(1)–Bi–Cl(2^{i})	91.2(1)	S–C(1)–N(1)	120(1)
Cl(1)–Bi–S	83.5(1)	S–C(1)–N(2)	127(1)
Cl(1)–Bi–S^{i}	177.7(1)	C(1)–N(1)–C(2)	112(1)
Cl(2)–Bi–Cl(2^{i})	174.2(2)	C(1)–N(2)–C(3)	111(1)
Cl(2)–Bi–S	89.1(1)	N(2)–C(3)–C(2)	104(1)
Cl(2)–Bi–S^{i}	87.0(1)	N(1)–C(2)–C(3)	101(1)

* $i = \bar{x}, y, \frac{1}{2} - z$.

$BiCl_3$·2etu, (2).—In $BiCl_3$·2etu the co-ordination at bismuth, which lies on a two-fold axis, is slightly distorted octahedral and involves two ethylenethiourea molecules co-ordinating through sulphur and four chloride ions, two of which are on a symmetry centre. The distortion of the octahedron is not very severe as indicated by the angles involving the *cis* atoms (83.5—98.7°) and by the *trans* angles (177.7 and 174.2°). No stereochemical influence of the Bi lone pair is observed. The Cl(1) chloride ion, which lies on a symmetry centre, bridges two adjacent bismuth atoms, so that the co-ordination polyhedra, sharing vertices, form infinite zigzag chains running along [001]. This arrangement resembles that found in bis(piperidinium) pentabromobismuthate(III).[15] On the other hand, in 2-methylpyridinium tetrabromo- and tetraiodo-bismuthate(III) [16] there are infinite chains of octahedra sharing edges.

---

[6] G. Fava Gasparri, A. Mangia, A. Musatti, and M. Nardelli, *Acta Cryst.*, 1968, **B24**, 367.

[7] L. Cavalca, M. Nardelli, and G. Branchi, *Acta Cryst.*, 1960, **13**, 688.

[8] L. Cavalca, M. Nardelli, and G. Fava Gasparri, *Acta Cryst.*, 1962, **15**, 1139.

[9] R. Grønbaek and S. E. Rasmussen, *Acta Chem. Scand.*, 1962, **16**, 2325.

[10] R. Grønbaek, *Acta Cryst.*, 1963, **16**, A65.

[11] A. Chiesi Villa, A. Gaetani Manfredotti, and C. Guastini, *Cryst. Struct. Comm.*, 1972, **1**, 125.

[12] G. D. Andreetti, P. Domiano, G. Fava Gasparri, M. Nardelli, and P. Sgarabotto, *Acta Cryst.*, 1970, **B26**, 1005.

[13] F. Hansen and R. Grønbaek Hazell, *Acta Chem. Scand.*, 1969, **23**, 1359.

[14] L. Coghi, A. M. Manotti Lanfredi, and A. Tiripicchio, *J.C.S. Perkin II*, 1976, 1808.

[15] W. G. McPherson and L. A. Meyers, *J. Phys. Chem.*, 1968, **72**, 532.

[16] B. K. Robertson, W. G. McPherson, and E. A. Meyers, *J. Phys. Chem.*, 1967, **71**, 3531.

TABLE 5

Bi–Cl and Bi–S distances (Å) in bismuth(III) compounds. Those marked with an asterisk involve bridging chloride

Compound	Bi–Cl		Bi–S	
$3BiCl_3\cdot4SC(NH_2)NHNH_2$ [a]	2.61(2)	2.74(2)	2.60(1)	
	2.66(1)	2.96(1) *	2.64(1)	
	2.68(1)	3.12(2) *		
$BiCl_3\cdot2SC(NHCH_2)_2$ [a]	2.703(5)		2.706(4)	
	2.859(2) *			
$3BiCl_3\cdot7SC(NH_2)_2$ [b]	2.677(10)	2.763(10)	2.680(6)	2.793(10)
	2.709(6)	2.934(6) *	2.700(6)	
	2.710(9)	2.939(6) *	2.763(10)	
$BiCl_3\cdot3SC(NH_2)_2$ [c]	2.714(8)		2.714(8)	
	2.728(3)		2.848(4)	
$BiPh(ONC_5H_4S)_2$ [d]			2.635(9)	2.712(6)
$BiCl_3(H_2NC_6H_4SO_2NHC_4H_2N_2OCH_3)_3$ [e]	2.529(8)			
$BiPh_3Cl_2$ [f]	2.530(17)	2.579(17)		
	2.560(17)	2.615(17)		
$Bi[S_2P(OPr^i)_2]_3$ [g]			2.690(6)	2.858(6)
			2.702(6)	2.878(6)
			2.714(6)	2.886(6)
$Bi_{12}Cl_{14}(BiCl_{1.167})$ [h]	2.617(50)	2.753(46)		
	2.666(35)	2.775(21)		
	2.730(34)	2.865(18)		
	2.743(37)	2.870(31)		

[a] Present work. [b] Ref. 1. [c] Ref. 2. [d] J. D. Curry and R. J. Jandacek, *J.C.S. Dalton*, 1972, 1120. [e] M. B. Ferrari, L. C. Capacchi, L. Cavalca, and G. F. Gasparri, *Acta Cryst.*, 1972, **B28**, 1169. [f] D. M. Hawley and G. Ferguson, *J. Chem. Soc.* (*A*), 1968, 2539. [g] S. L. Lawton, C. J. Fuhrmeister, R. G. Haas, C. S. Jarman, jun., and F. G. Lohmeyer, *Inorg. Chem.*, 1974, **13**, 135. [h] A. Hershaft and J. D. Corbett, *Inorg. Chem.*, 1963, **2**, 979.

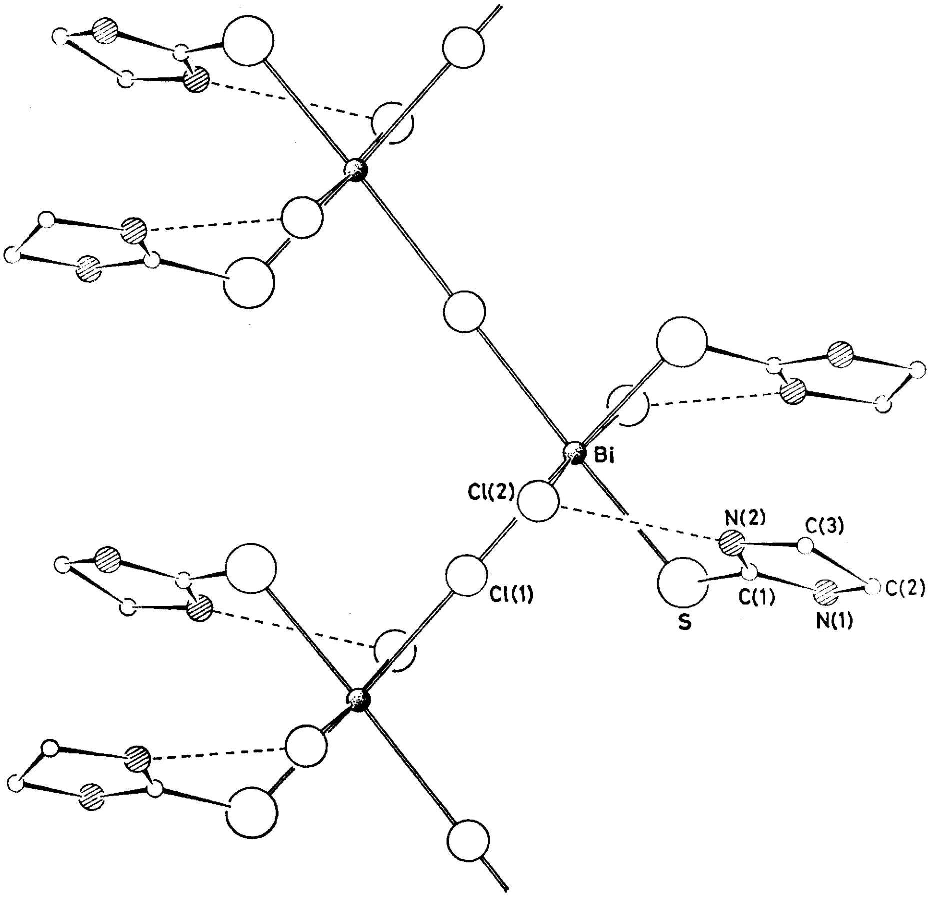

FIGURE 2 Clinographic projection of complex (2)

Bond distances and angles are in Table 4, and in Table 5 Bi–Cl and Bi–S distances in some bismuth compounds are compared. As observed for structure (1), the Bi–Cl distance involving the bridging chlorine in (2) is also significantly longer than the others. The interatomic distances in the ethylenethiourea molecule agree reasonably well with those found in other etu complexes [17-20] and in etu itself.[21] The orientation of the etu molecules is determined by the interaction N(2) · · · Cl(2) (3.26 Å) which probably involves the hydrogen atom attached to N(2).

Packing of the chains is mainly determined by the Cl(2) · · · HN(1^i) (3.24 Å; $i = \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$) contact which can be considered as a hydrogen bond [Cl(2)–N(1^i)–C(2^i) 127.5, Cl(2)–N(1^i)–C(1^i) 120.4°].

[7/1364 *Received, 27th July*, 1977]

---

[17] L. P. Battaglia, A. Bonamartini Corradi, M. Nardelli, and M. E. Vidoni Tani, *J.C.S. Dalton*, 1976, 143.

[18] M. Nardelli, G. Fava, A. Musatti, and A. Manfredotti, *Acta Cryst.*, 1966, **21**, 910.

[19] L. Cavalca, M. Nardelli, and G. Fava, *Acta Cryst.*, 1960, **13**, 125.

[20] M. S. Weininger, G. W. Hunt, and E. L. Amma, *J.C.S. Chem. Comm.*, 1972, 1140.

[21] P. Wheatley, *Acta Cryst.*, 1953, **6**, 369.