Cationic and Anionic Bismuth(III) in Chloro-thiourea Complexes: Crystal Structure of $[Bi(tu)_6][Bi\{(tu)_{1.5}Cl_{1.5}\}Cl_3]_2$ (tu = thiourea)

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The structure of the title compound (I) has been solved from diffractometer data by the heavy-atom technique and refined by least-squares methods to R 0.043 for 1 513 observed reflections. Crystals are rhombohedral, with unit-cell dimensions a = 13.54(1), c = 7.07(1) Å. The structure consists of $[Bi\{(tu)_{1.5}Cl_{1.5}\}Cl_3]^{3/2-}$ (tu = thiourea) anions, in which there is disorder involving thiourea and chlorine atoms, and $[Bi(tu)_6]^{3+}$ cations. In both ions bismuth atoms occupy special positions in space group $P\bar{3}$ and bond octahedrally to thiourea and (or) chlorine ions. A detailed comparison between this compound and $3BiCl_3{\cdot}7tu$ is made.

BISMUTH TRICHLORIDE and thiourea (tu) have been reported to give two adducts corresponding to the molar ratios $BiCl_3$: tu of 2 : 1 and 1 : 3, and it was suggested that the second occurs in two modifications, one yellow (m.p. 180 °C), the other red (m.p. 186 °C).[1] *X*-Ray crystal-structure determinations of these two modifications showed them to be two different compounds of molar ratios 3 : 7 (II; yellow form),[2] and 1 : 3 (I; red form); the structure of the red form is reported here.

Further interest arose in defining the role played by bismuth in these compounds, since the *X*-ray analysis showed bismuth(III) to be present in both complex anion and cation.

EXPERIMENTAL

Preparation.—An excess of thiourea was added to a solution of $BiCl_3$ (0.01 mol) in 2N-HCl. After 2 h red prismatic crystals of (I) were obtained. From the filtered solution, the yellow crystalline product (II) was formed after 2 days.

Crystal Data.—$C_3H_{12}BiCl_3N_6S_3$, M = 543.7, Rhombohedral, a = 13.54(1), c = 7.07(1) Å, U = 1 123 Å^3, D_m = 2.49 g cm^{-3}, Z = 3, D_c = 2.46 g cm^{-3}, $F(000)$ = 762. Mo-K_α radiation, λ = 0.7107 Å; μ(Mo-K_α) = 121.0 cm^{-1}. Space group $P\bar{3}$ (from structural analysis). Unit-cell dimensions were first determined from rotation and Weissenberg photographs and then refined by single-crystal diffractometry.

Data Collection.—Three-dimensional intensity data were collected on an automated Siemens AED single-crystal diffractometer, by use of niobium-filtered Mo-K_α radiation and the ω—2θ scanning technique. The crystal used was mounted with the c axis coincident with the ϕ axis of the instrument, and was 0.21 × 0.16 × 0.26 mm. Of 1 966 independent reflections measured in the range $6° < 2\theta < 56°$, 1 513 were considered observed having $I \geqslant 2\sigma(I)$, and used in subsequent calculations. The intensity of a standard reflection measured periodically every 20 reflections was essentially constant during data collection.

Intensity data were reduced to structure amplitudes by application of Lorentz and polarization factors. No correction for absorption was made. Data were placed on an absolute scale by correlating observed and calculated values.

Structure Determination and Refinement.—The structure was solved by the heavy-atom technique, the initial set of co-ordinates for the bismuth atoms being deduced from a Patterson map. The electron-density distribution, calculated with the phases of the bismuth atoms, gave the positions of all non-hydrogen atoms except of the disordered thiourea molecules, which were found successively, with a 50% population, from a difference-Fourier map. Refinement was by block-diagonal least-squares, with anisotropic thermal parameters, to R 4.3%. No attempt was made to locate the hydrogen atoms.

Table 1 lists positional parameters with their estimated standard deviations. Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21959 (10 pp., 1 microfiche).† Atomic scattering factors were taken from ref. 3.

TABLE 1

Final atomic fractional co-ordinates (× 10^4), with estimated standard deviations in parentheses

	x/a	*y/b*	*z/c*
Bi(1)	0	0	0
Bi(2)	3 333	6 666	7 520(1)
Cl(1)	4 816(2)	6 291(2)	9 586(4)
Cl(2)	2 889(5)	4 840(5)	5 340(9)
S(1)	656(2)	1 972(2)	2 264(4)
S(2)	2 889(5)	4 840(5)	5 340(9)
N(1)	2 636(8)	3 602(8)	968(14)
N(2)	2 707(9)	2 259(9)	2 806(15)
N(3)	4 390(19)	4 168(19)	6 203(31)
N(4)	4 995(18)	5 606(17)	4 072(29)
C(1)	2 113(9)	2 659(9)	1 979(14)
C(2)	4 201(17)	4 886(17)	5 231(28)

All calculations were performed on a Cyber 76 computer at the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale.

RESULTS AND DISCUSSION

As found in the yellow compound (II), di-μ-chloro-bis[chlorotri(thiourea)bismuth(III)] pentachloro(thiourea)bismuthate(III),[2] in the present red one (I) there are also two kinds of chemically non-equivalent bismuth atoms, which are octahedrally surrounded by chlorine ions and (or) thiourea (tu) molecules. The structure is quite unexpected because the chemical formula had suggested a neutral complex, with three chlorine ions

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† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

[1] Gmelins ' Handbuch der Anorganischen Chemie,' 8 auflage, 1964, **19**, 684.

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

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

and three thiourea molecules co-ordinated to bismuth atom, as in trichlorotris(6-methoxy-3-sulphanilamidopyridazine)bismuth.[4] However, this present structure is built of $[Bi\{(tu)_{1.5}Cl_{1.5}\}Cl_3]^{\frac{3}{2}-}$ anions and $[Bi(tu)_6]^{3+}$ cations [Figure (2)], which occupy special positions in the space group $P\bar{3}$, *i.e.* the anion at $\frac{1}{3},\frac{2}{3},z$ on a three-fold axis, the cation at 0,0,0 on a $\bar{3}$ inversion axis. As in (II), the anion is disordered, but this disorder now involves three chloride ions and three tu molecules as required by symmetry, so that the anion is either $[BiCl_6]^{3-}$ or $BiCl_3$-$(tu)_3$. In the cation the six thiourea molecules co-ordinate to the metal with an arrangement of sulphur ligands resembling that found in *OO'*-di-isopropyl phosphorodithioatobismuth(III).[5]

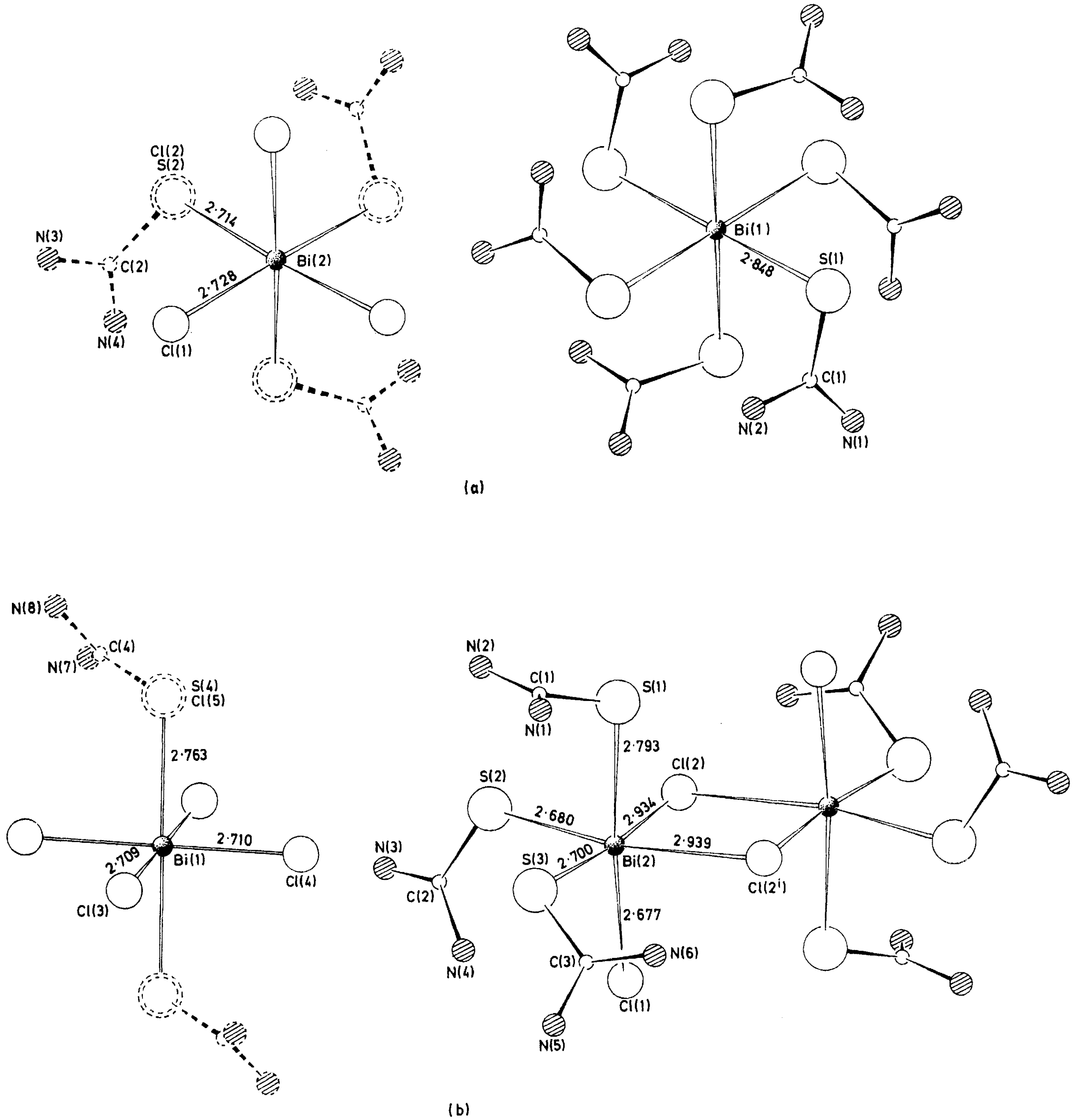

FIGURE 1 Comparison of co-ordination polyhedron (a) the red (I) and (b) the yellow (II) derivative

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[4] M. Belicchi Ferrari, L. Calzolari Capacchi, L. Cavalca, and G. Fava Gasparri, *Acta Cryst.*, 1972, **B28**, 1169.

[5] S. L. Lawton, C. J. Fuhrmeister, R. H. Haas, C. S. Jarman, jun., and F. G. Lohmeyer, *Inorg. Chem.*, 1974, **13**, 135.

Comparison of the bismuth co-ordination polyhedra in (I) and (II) [Figure 1] shows that in both the lone pair exerts no stereochemical influence; this is not especially unusual, more examples being known when the lone pair is stereochemically inactive rather than active.[6] In particular many structures of AX_6E systems (A = central atom, X = ligand, E = unshared electron pair) are known where the lone pair is inactive and the ligands in them are chlorine ions or sulphur atoms of thiourea derivatives.

TABLE 2

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

(*a*) Distances

Bi(1)–S(1)	2.848(4)	Bi(2)–S(2), Cl(2)	2.714(8)
S(1)–C(1)	1.72(1)	Bi(2)–Cl(1)	2.728(3)
C(1)–N(1)	1.32(2)	S(2)–C(2)	1.75(2)
C(1)–N(2)	1.31(2)	C(2)–N(3)	1.32(4)
		C(2)–N(4)	1.32(3)

(*b*) Angles

S(1)–Bi(1)–S(1^{I})	91.5(1)	Cl(1)–Bi(2)–S(2), Cl(2)	89.0(2)
Bi(1)–S(1)–C(1)	100.2(4)	Cl(1)–Bi(2)–S(2^{II}), Cl(2^{II})	86.0(2)
S(1)–C(1)–N(1)	120.2(9)	Cl(1)–Bi(2)–S(2^{III}), Cl(2^{III})	177.0(3)
S(1)–C(1)–N(2)	119.9(9)	Bi(2)–S(2)–C(2)	103.5(8)
N(1)–C(1)–N(2)	120(1)	S(2)–C(2)–N(3)	121(2)
N(3)–C(2)–N(4)	119(2)	S(2)–C(2)–N(4)	120(2)

Roman numeral superscripts denote the following equivalent positions, relative to the reference molecule at x, y, z:

I $\bar{y}, x - y, z$ III $y - x, \bar{x}, z - 1$
II $1 - y, x - y, z - 1$

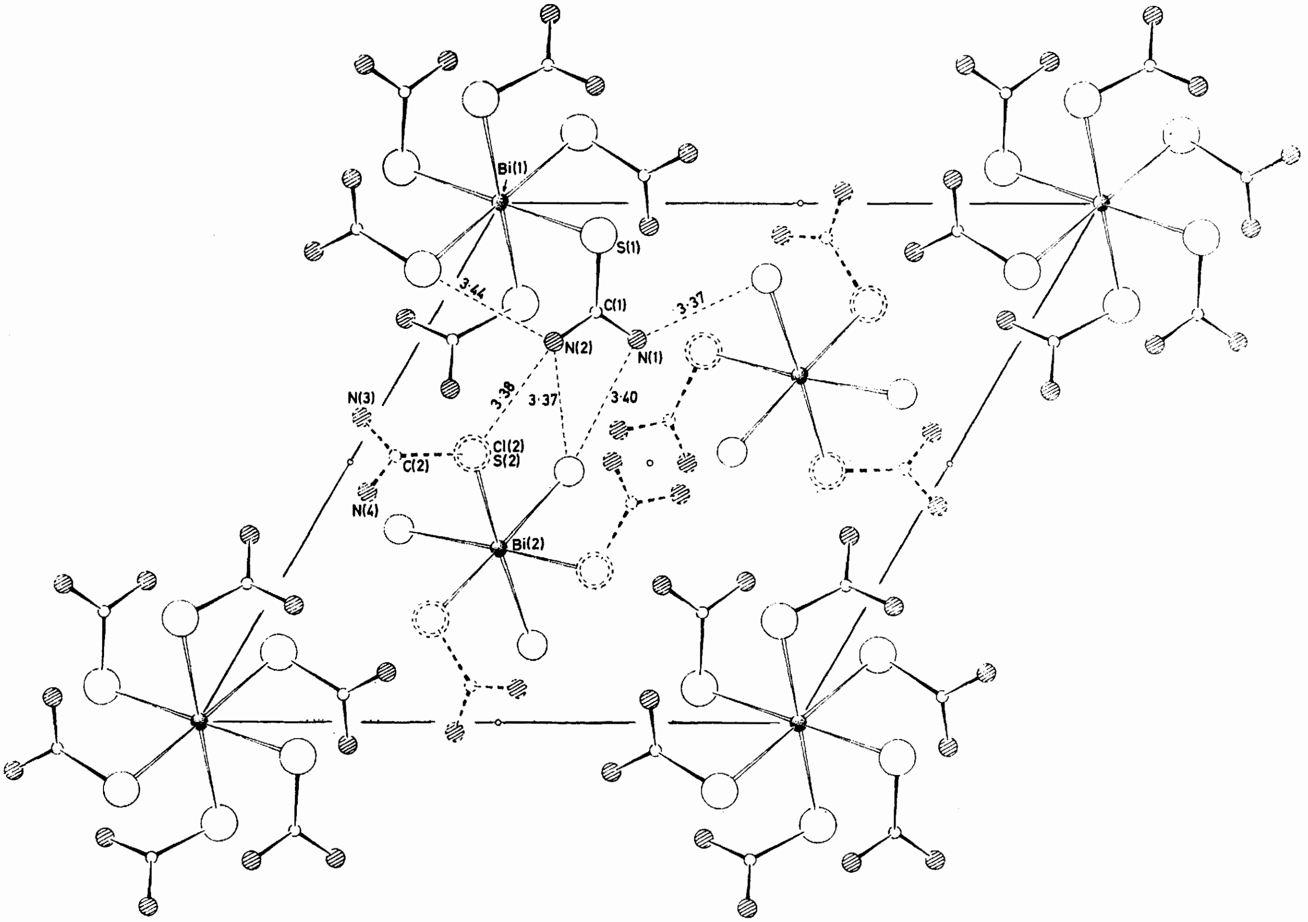

FIGURE 2 Projection of the structure of (I) on [001]; dashed lines indicate S · · · N interactions and possible hydrogen bonds

Table 2 lists bond lengths and angles for the red compound (I). As far as bond angles in the co-ordination polyhedra are concerned, a comparable situation is found in the anionic parts of the red and yellow compounds, with a nearly regular octahedral environment of the metal atom: the angles involving atoms mutually *cis* are 90.4, 90.6, 92.6° in (II) and 86.0 and 89.0° in (I), while the *trans* angles are 180° for symmetry requirements in (II) and 177.0° in (I). However, there are differences between the two cations: the presence of bridging chlorine ions seems to be responsible for the rather large distortions (84.2—104.0° for the *cis* angles, 168.1, 170.2, 175.1° for the *trans* angles) observed in the cation of (II) compared with those in (I) (91.5 *cis* and 180° *trans*).

As pointed out by Lazarini *et al.*,[7] several polynuclear bismuth complexes with bridging halogens have been observed, but the yellow compound seems to be one of the few in which bridging is made by chlorine. However, as far as we know, Bi–Cl bonds are only present in some bismuth chlorides *e.g.* bismuth chloride, $Bi_{24}Cl_{28}$ (2.60—

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[6] K. J. Wynne, *J. Chem. Educ.*, 1973, **50**, 328.

[7] F. Lazarini, L. Golic, and G. Pelizzi, *J. Cryst. Mol. Structure*, in the press.

2.87 Å),[8] bismuth subchloride, $Bi_{12}Cl_{14}$ (2.61—2.87 Å),[9] bismuth trichloride (2.47—2.52 Å),[10] and in trichlorotris(6-methoxy-3-sulphanilamidopyridazine)bismuth (2.599 Å),[4] and in $[Co(NH_3)_6][BiCl_6]$ (2.52 Å).[11] In the present compound the Bi–Cl bond lengths (2.714 and 2.728 Å) agree fairly well with those involving terminal chlorines in the yellow compound (2.677—2.763 Å).

The Bi–S distances in the two compounds vary from 2.680 to 2.848 Å and this range is practically the same as that observed in *OO'*-di-isopropyl phosphorodithioatobismuth(III) (2.690—2.886 Å).[5]

The atomic co-ordinates for light atoms in structures containing atoms as heavy as bismuth have necessarily quite low accuracy, so the structural parameters for thioureas, and in particular those for the disordered molecules, show a poor degree of reliability. As found in the yellow derivative, packing is mainly determined by Cl · · · N and S · · · N interactions (Figure 2), some of which can be regarded as hydrogen bonds.

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[8] A. Hershaft and J. D. Corbett, *J. Chem. Phys.*, 1962, **36**, 551.

[9] A. Hershaft and J. D. Corbett, *Inorg. Chem.*, 1963, **2**, 979.

[10] S. C. Nyburg, G. A. Ozin, and J. T. Szymański, *Acta Cryst.*, 1971, **B27**, 2298.

[11] M. Atoji and T. Watanabè, *J. Chem. Phys.*, 1957, **20**, 1045.