# Structural Investigations on Bismuth–Thiourea Derivative Adducts: Crystal Structures of Tetra[1-allyl-3-(2-pyridyl)thiourea-*S*]di-μ-chloro-tetrachlorodibismuth(III) and Hexa[1-allyl-3-(2-pyridyl)thiourea-*S*]bismuth(III) Nitrate

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The crystal structures of $[\{BiCl_3(aptu)_2\}_2]$ (1) [aptu = 1-allyl-3-(2-pyridyl)thiourea-*S*] and of $[Bi(aptu)_6][NO_3]_3$ (2) have been determined from three-dimensional *X*-ray data and refined by least-squares methods to $R = 0.056$ and 0.092 respectively. Both crystals are triclinic with unit-cell dimensions: (1), $a = 12.903(10)$, $b = 11.084(10)$, $c = 9.739(10)$ Å, $\alpha = 109.8(1)$, $\beta = 97.5(1)$, $\gamma = 107.3(1)°$, $Z = 1$, space group $P\bar{1}$; (2), $a = 13.104(10)$, $b = 15.296(10)$, $c = 11.591(10)$ Å, $\alpha = 126.7(1)$, $\beta = 109.1(1)$, $\gamma = 92.4(1)°$, $Z = 1$, space group $P\bar{1}$. The structure of (1) consists of a binuclear centrosymmetric neutral complex, in which each bismuth atom is surrounded by two sulphurs of the ligand molecules and two chlorine atoms; two other chlorines, forming asymmetrical bridges, complete the distorted octahedral co-ordination. In (2) $[Bi(aptu)_6]^{3+}$ and $NO_3^-$ ions are present. The heavy atom, lying on the centre of symmetry at the origin of the cell, is surrounded by six sulphur atoms from aptu molecules which are arranged in approximate $\bar{3}$ symmetry to give a distorted octahedral co-ordination.

As a result of our investigations into $BiCl_3$ adducts with sulphur-containing compounds of the thiourea type we have reported in previous papers the crystal structures of two complexes with thiourea,[1,2] and subsequently the adducts with ethylenethiourea and thiosemicarbazide.[3] The present work reports the results of the structural analyses of the adducts $[\{BiCl_3(aptu)_2\}_2]$ (1) [aptu = 1-allyl-3-(2-pyridyl)thiourea-*S*] and $[Bi(aptu)_6][NO_3]_3$ (2), and shows that a neutral binuclear complex is formed in (1) while in (2) discrete $[Bi(aptu)_6]^{3+}$ and nitrate ions are present; a comparison between these compounds and the two thiourea adducts is made.

## EXPERIMENTAL

Both complexes were prepared following the procedure of Ahmed and Mandal [4] and recrystallized from chloroform. Yellow prisms were obtained for (1) and red platelets for (2).

*Crystal Data.*—*Complex* (1). $C_{36}H_{44}Bi_2Cl_6N_{12}S_4$, $M = 1\,403.9$, Triclinic, $a = 12.903(10)$, $b = 11.084(10)$, $c = 9.739(10)$ Å, $\alpha = 109.8(1)$, $\beta = 97.5(1)$, $\gamma = 107.3(1)°$, $U = 1\,209(2)$ Å$^3$, $D_m = 1.91$ g cm$^{-3}$, $Z = 1$, $D_c = 1.93$ g cm$^{-3}$, $F(000) = 670$, Mo-$K_\alpha$ radiation ($\lambda = 0.710\,69$ Å), $\mu$(Mo-$K_\alpha$) = 75.0 cm$^{-1}$, space group $P\bar{1}$ (from structural analysis).

*Complex* (2). $C_{54}H_{66}BiN_{21}O_9S_6$, $M = 1\,554.6$, Triclinic, $a = 13.104(10)$, $b = 15.296(10)$, $c = 11.591(10)$ Å, $\alpha = 126.7(1)$, $\beta = 109.1(1)$, $\gamma = 92.4(1)°$, $U = 1\,674(4)$ Å$^3$, $D_m = 1.55$ g cm$^{-3}$, $Z = 1$, $D_c = 1.54$ g cm$^{-3}$, $F(000) = 788$, Mo-$K_\alpha$ radiation ($\lambda = 0.710\,69$ Å), $\mu$(Mo-$K_\alpha$) = 28.7 cm$^{-1}$, space group $P\bar{1}$ (from structural analysis).

Cell dimensions were obtained, first from rotation and Weissenberg photographs, and then refined by single-crystal diffractometry.

*Data Collection.*—Three-dimensional intensity data were collected on an automatic Siemens AED single-crystal diffractometer using niobium-filtered Mo-$K_\alpha$ radiation and the $\omega$—2$\theta$ scan technique. The crystals of dimensions $0.065 \times 0.179 \times 0.326$ mm for (1) and $0.098 \times 0.261 \times 0.228$ mm for (2) were mounted with the *c* axis coincident with the $\phi$ axis of the instrument: 2 842 for (1) and 6 247 for (2) independent reflections in the ranges $6 < 2\theta < 44°$ and $6 < 2\theta < 52°$ respectively were collected. Of these, 2 561 and 3 427 having $I > 2\sigma(I)$ were considered 'observed.' During the data collection a standard reflection was measured every 20 reflections to check the instrument and crystal alignment: its intensity was practically constant.

Intensity data were reduced to structure amplitudes by application of Lorentz and polarization factors, while correction for absorption was applied only to the data of (1); its transmission factors ranged from 0.17 to 0.65.

*Structure Analysis.*—The structures were solved by the heavy-atom technique deducing the initial co-ordinates of bismuth from a Patterson map for (1), while for (2), where $Z = 1$, the bismuth was placed on the centre of symmetry at the origin so that the first Fourier was enough to give a starting model of the structure. All the non-hydrogen atoms were located from Fourier syntheses phased by bismuth. Both refinements were carried out by full-matrix least squares with anisotropic thermal parameters and anomalous dispersion correction for Bi, Cl, and S; the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with $w = 1/[\sigma^2(F_o) + gF_o^2]$, $g = 8.6 \times 10^{-3}$ for (1) and $5.0 \times 10^{-3}$ for (2). No attempts were made to locate the hydrogen atoms in either structure. Tables 1 and 2 show the positional parameters with their estimated standard deviations for (1) and (2) respectively; the location of the terminal carbon atoms of the allyl groups and the nitrate ions in (2) is rather poor as a consequence of a large thermal motion (or disorder) and the presence of the heavy bismuth atom. The atomic scattering factors were those of Cromer and Mann.[5] 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 [6] with financial support from the University of Parma. Observed and calculated structure factors and thermal parameters are available as Supplementary Publication No. SUP 22868 (39 pp.).†

## DISCUSSION

As shown in Figure 1, the structure of $[\{BiCl_3(aptu)_2\}_2]$ (1) consists of a binuclear centrosymmetric neutral complex in which two sulphur atoms from two ligand

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

TABLE 1

Final fractional co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for (1)

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Bi | 1 623(1) | 608(1) | 1 120(1) |
| Cl(1) | 2 299(3) | −1 474(3) | 1 215(5) |
| Cl(2) | 2 711(4) | 1 949(4) | 3 826(4) |
| Cl(3) | −426(3) | −118(3) | 2 071(4) |
| S(1) | 1 049(4) | 2 844(4) | 1 133(4) |
| S(2) | 3 405(3) | 1 737(5) | 126(5) |
| N(1) | 1 777(11) | 5 186(12) | 3 637(13) |
| N(2) | 678(9) | 3 191(10) | 3 837(12) |
| N(3) | 1 191(10) | 5 116(11) | 6 143(12) |
| N(4) | 5 618(11) | 2 603(12) | 1 047(14) |
| N(5) | 4 640(10) | 852(11) | 1 686(13) |
| N(6) | 6 596(10) | 1 513(11) | 2 627(13) |
| C(1) | 1 203(12) | 3 828(13) | 2 986(15) |
| C(2) | 2 434(15) | 5 999(17) | 2 929(20) |
| C(3) | 3 655(18) | 6 373(19) | 3 527(22) |
| C(4) | 4 131(20) | 6 008(22) | 4 566(26) |
| C(5) | 722(11) | 3 775(12) | 5 399(14) |
| C(6) | 271(12) | 2 830(14) | 6 049(16) |
| C(7) | 283(14) | 3 397(15) | 7 560(18) |
| C(8) | 757(14) | 4 816(15) | 8 364(17) |
| C(9) | 1 201(12) | 5 634(14) | 7 626(16) |
| C(10) | 4 650(13) | 1 752(14) | 1 020(16) |
| C(11) | 5 747(16) | 3 643(18) | 372(20) |
| C(12) | 6 051(23) | 5 033(26) | 1 742(28) |
| C(13) | 6 828(27) | 6 130(31) | 1 946(34) |
| C(14) | 5 563(12) | 729(13) | 2 478(15) |
| C(15) | 5 285(13) | −226(15) | 3 178(17) |
| C(16) | 6 191(14) | −326(16) | 4 010(18) |
| C(17) | 7 260(15) | 452(16) | 4 115(19) |
| C(18) | 7 434(14) | 1 375(16) | 3 395(18) |

molecules and four chlorine atoms co-ordinate to each bismuth atom, the resulting co-ordination being distorted octahedral. Two chlorine atoms, related by a centre of symmetry, are bridging, so that the two octahedra share an edge. The co-ordination polyhedron is rather distorted as indicated by the values of the angles formed by adjacent atoms, which range from 68.8(2) to 113.5(2)° (Table 3); the largest deviations from the theoretical values involve the chlorine bridging atoms. The conformation of these dimers partially resembles that of the binuclear cation $[\{BiCl_2(tu)_3\}_2]^{2+}$ (tu = thiourea) found in the crystal of the ' yellow compound ' [1] $[Bi_3Cl_9(tu)_7]$ (3). In the compounds (1) and (3) two adjacent octahedra share an edge occupied by two centrosymmetric chlorine atoms, however, the bridges formed are practically symmetrical in (3) but asymmetrical in (1). In both the octahedra of (1) and (3) the sulphur atoms are *cis* and the Bi–S bonds approximately normal to the bridging plane [Bi(2)–S(1) = 2.793(10) Å in (3) and Bi–S(1) = 2.786(6) Å in (1)] are significantly longer than the others. The lengths of these Bi–S bonds and the Bi–Cl(3) bridging bonds (Table 3) agree with those previously found in similar compounds,[3] while the terminal Bi–Cl(2) = 2.503(5) Å distance is rather short, although comparable values have been found in compounds such as triphenylbismuth dichloride [7] 2.530(17) Å, trichlorotris(6-methoxy-3-sulphanilamidopyridazine)bismuth(III) [8] 2.529(8) Å, $BiCl_3$ [9] 2.468(4), 2.513(7), 2.518(7) Å, and ferrocenium tetrachlorobismuthate [10] 2.522(3) Å. This value lies in the range 2.47—2.52 Å assigned by Mammano *et al.*[10] to the Bi–Cl ' single bond ' in agreement with

TABLE 2

Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for (2)

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Bi | 0(0) | 0(0) | 0(0) |
| S(1) | 1 964(4) | −278(4) | −470(6) |
| S(2) | 843(5) | 803(5) | 3 137(8) |
| S(3) | 1 020(6) | 2 316(5) | 1 666(8) |
| O(1) | 2 714(26) | −2 282(25) | 226(35) |
| O(2) | 1 683(20) | −3 253(23) | 365(29) |
| O(3) | 1 843(21) | −1 505(23) | 1 470(31) |
| O(4) | 4 964(43) | 5 952(44) | 5 844(59) |
| O(5) | 4 980(61) | 4 498(74) | 5 602(93) |
| O(6) | 4 995(35) | 4 714(35) | 3 700(49) |
| N(1) | 3 236(14) | 554(14) | 2 372(21) |
| N(2) | 4 757(16) | 2 225(17) | 4 618(24) |
| N(3) | 3 660(15) | 1 684(15) | 1 817(22) |
| N(4) | −100(14) | −1 248(15) | 2 161(21) |
| N(5) | −1 590(18) | −1 950(19) | 2 289(26) |
| N(6) | −816(16) | 196(16) | 3 626(22) |
| N(7) | −387(13) | 3 017(13) | 3 003(19) |
| N(8) | −128(13) | 4 176(13) | 5 617(19) |
| N(9) | 1 496(15) | 3 688(15) | 4 727(21) |
| N(10) | 2 025(21) | −2 429(22) | 555(29) |
| N(11) | 5 000(0) | 5 000(0) | 5 000(0) |
| C(1) | 3 050(17) | 771(18) | 1 401(26) |
| C(2) | 4 061(18) | 1 257(19) | 4 053(27) |
| C(3) | 4 033(24) | 901(24) | 4 791(36) |
| C(4) | 4 828(27) | 1 579(28) | 6 454(39) |
| C(5) | 5 572(24) | 2 605(25) | 7 071(35) |
| C(6) | 5 510(25) | 2 874(26) | 6 189(39) |
| C(7) | 3 493(22) | 1 938(23) | 796(33) |
| C(8) | 4 353(34) | 1 790(34) | 72(47) |
| C(9) | 5 083(41) | 1 346(42) | 188(57) |
| C(10) | −123(18) | −98(18) | 2 876(26) |
| C(11) | −863(18) | −2 153(18) | 1 727(26) |
| C(12) | −634(22) | −3 208(23) | 840(32) |
| C(13) | −1 372(28) | −4 119(28) | 423(40) |
| C(14) | −2 177(27) | −3 969(28) | 994(38) |
| C(15) | −2 322(28) | −2 884(29) | 1 832(40) |
| C(16) | −921(22) | 1 393(22) | 4 421(31) |
| C(17) | −1 809(41) | 1 445(39) | 4 857(53) |
| C(18) | −2 705(57) | 1 057(57) | 4 418(77) |
| C(19) | 715(17) | 3 093(17) | 3 265(25) |
| C(20) | −847(16) | 3 519(16) | 4 092(24) |
| C(21) | −2 013(19) | 3 279(19) | 3 510(27) |
| C(22) | −2 454(20) | 3 785(20) | 4 625(29) |
| C(23) | −1 731(21) | 4 469(21) | 6 200(31) |
| C(24) | −575(19) | 4 670(19) | 6 716(27) |
| C(25) | 2 709(25) | 3 765(26) | 5 156(36) |
| C(26) | 3 528(33) | 4 591(37) | 6 904(51) |
| C(27) | 3 313(46) | 5 264(50) | 7 925(70) |

TABLE 3

Bond distances (Å) and angles (°) with their estimated standard deviations in the co-ordination polyhedron and thiourea moieties for (1)

| | | | |
|---|---|---|---|
| Bi–Cl(1) | 2.723(5) | S(1)–C(1) | 1.71(1) |
| Bi–Cl(2) | 2.503(5) | S(2)–C(10) | 1.72(2) |
| Bi–Cl(3) | 2.894(5) | C(1)–N(1) | 1.34(2) |
| Bi–Cl(3$^{I}$) * | 3.073(5) | C(1)–N(2) | 1.38(2) |
| Bi–S(1) | 2.786(6) | C(10)–N(4) | 1.31(2) |
| Bi–S(2) | 2.735(6) | C(10)–N(5) | 1.36(2) |
| Cl(1)–Bi–Cl(3) | 99.5(2) | S(1)–Bi–Cl(3$^{I}$) | 68.8(2) |
| Cl(1)–Bi–Cl(3$^{I}$) | 113.5(2) | S(1)–Bi–S(2) | 84.9(2) |
| Cl(1)–Bi–Cl(2) | 87.4(2) | S(2)–Bi–Cl(3$^{I}$) | 79.0(2) |
| Cl(1)–Bi–S(2) | 93.3(2) | Bi–S(1)–C(1) | 106.2(6) |
| Cl(1)–Bi–S(1) | 176.8(2) | Bi–S(2)–C(10) | 113.1(6) |
| Cl(2)–Bi–Cl(3) | 89.8(2) | S(1)–C(1)–N(1) | 123(1) |
| Cl(2)–Bi–Cl(3$^{I}$) | 157.5(2) | S(1)–C(1)–N(2) | 118(1) |
| Cl(2)–Bi–S(1) | 90.0(2) | N(1)–C(1)–N(2) | 118(1) |
| Cl(2)–Bi–S(2) | 92.1(2) | S(2)–C(10)–N(4) | 121(1) |
| Cl(3)–Bi–S(1) | 82.4(2) | S(2)–C(10)–N(5) | 120(1) |
| Cl(3)–Bi–Cl(3$^{I}$) | 94.6(2) | N(4)–C(10)–N(5) | 119(2) |
| Cl(3)–Bi–S(2) | 167.2(2) | | |
| Bi–Cl(3)–Bi$^{I}$ | 85.4(1) | | |

* I = $\bar{x}, \bar{y}, \bar{z}$

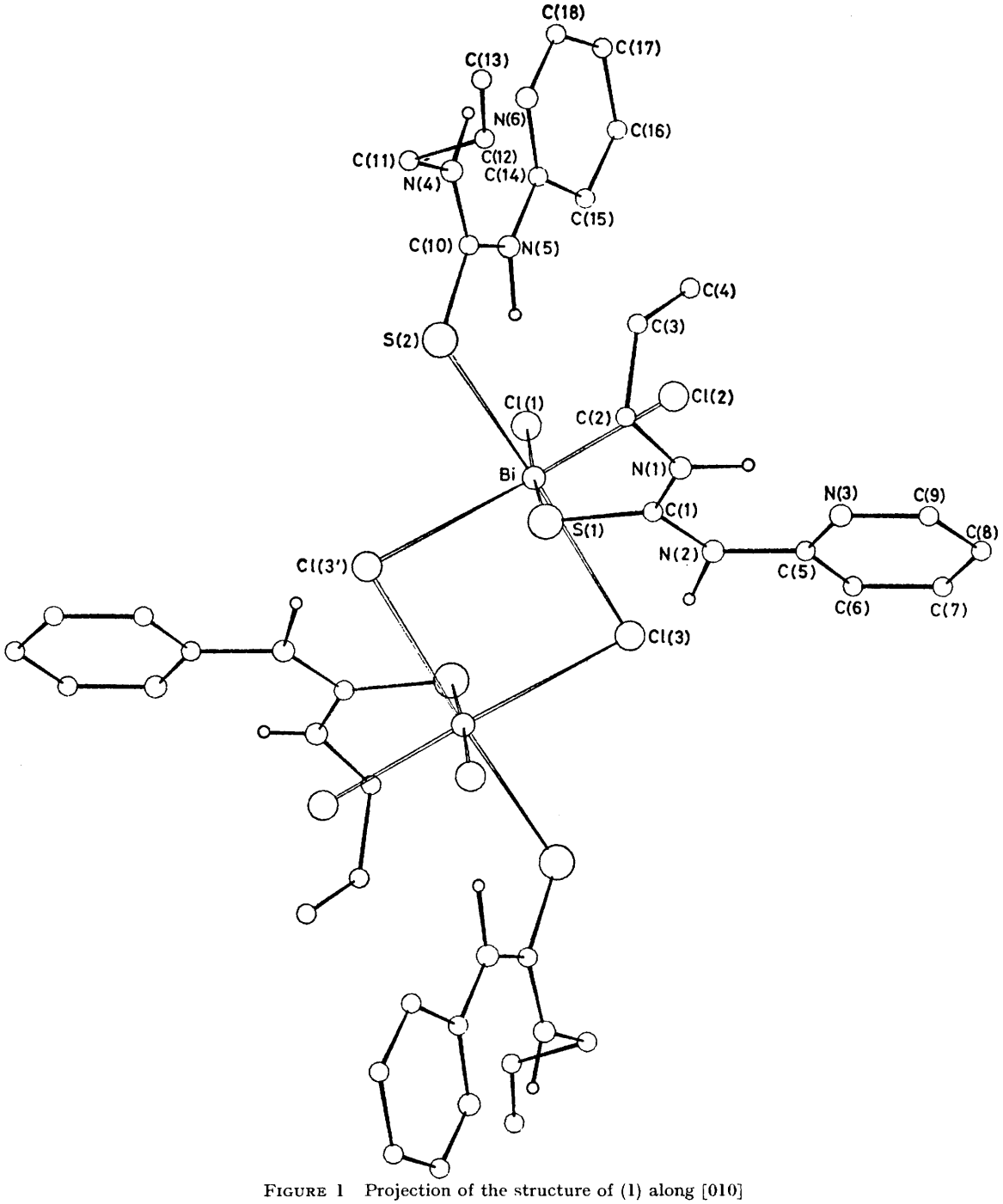


FIGURE 1 Projection of the structure of (1) along [010]

the fact that in the present complex the Cl(2) atom is not involved in short contacts or hydrogen bonds.

Bond distances and angles in the two ligand molecules are normal. The pyridine rings and the thiourea molecules are planar within experimental error and in each ligand are almost coplanar, the angles formed by their weighted least-squares planes being only 7.7° [between S(1)C(1)N(1)N(2) and N(3)—C(5)] and 3.9° [between S(2)C(10)N(4)N(5) and N(6)—C(14)]

* Hydrogen atoms are in calculated positions 1.00 Å from their corresponding nitrogens.

The structure is packed by van der Waals interactions [Table 4(*a*)] and by intramolecular contacts which can be considered as hydrogen bonds.*

| | | |
|---|---|---|
| N(1) · · · N(3) | 2.67(2) Å | N(1)–H · · · N(3) = 133° |
| N(4) · · · N(6) | 2.66(2) Å | N(4)–H · · · N(6) = 132° |
| N(5) · · · Cl(1) | 3.19(1) Å | N(5)–H · · · Cl(1) = 171° |
| N(2) · · · Cl(3) | 3.23(1) Å | N(2)–H · · · Cl(3) = 165° |

The structure of $[Bi(aptu)_6][NO_3]_3$ (2) shows the presence of discrete $[Bi(aptu)_6]^{3+}$ cations (Figure 2) and nitrate ions. The bismuth atom, lying on the centre of

TABLE 4

Some contacts less than 3.50 Å for (1) and (2)

(*a*) For (1)

| | | | |
|---|---|---|---|
| Cl(2) · · · C(1) | 3.46(2) | C(9) · · · N($2^{II}$) | 3.44(2) |
| S(1) · · · Cl($3^{I}$) | 3.32(1) | C(9) · · · C($1^{III}$) | 3.35(3) |
| N(3) · · · N($2^{II}$) | 3.47(2) | C(14) · · · C($10^{III}$) | 3.49(2) |
| N(3) · · · N($3^{II}$) | 3.44(2) | | |

(*b*) For (2) excluding nitrate ions

| | | | |
|---|---|---|---|
| C(24) · · · C($19^{II}$) | 3.42(5) | N(8) . . . C($20^{II}$) | 3.48(4) |
| C(24) · · · N($7^{II}$) | 3.49(4) | C(27) · · · C($14^{IV}$) | 3.41(9) |

I = $\bar{x}$, $\bar{y}$, $\bar{z}$; II = $\bar{x}$, 1 − $y$, 1 − $z$; III = 1 − $x$, $\bar{y}$, $\bar{z}$; IV = $\bar{x}$, $\bar{y}$, 1 − $z$.

TABLE 5

Bond distances (Å) and angles (°) with their estimated standard deviations in parentheses in the co-ordination polyhedron and thiourea groups for (2)

| | | | |
|---|---|---|---|
| Bi–S(1) | 2.798(6) | S(2)–C(10) | 1.64(3) |
| Bi–S(2) | 2.808(10) | C(10)–N(4) | 1.44(3) |
| Bi–S(3) | 2.797(9) | C(10)–N(6) | 1.37(4) |
| S(1)–C(1) | 1.72(2) | S(3)–C(19) | 1.70(3) |
| C(1)–N(1) | 1.31(5) | C(19)–N(7) | 1.36(3) |
| C(1)–N(3) | 1.29(4) | C(19)–N(9) | 1.30(3) |
| S(1)–Bi–S(2) | 99.6(3) | N(1)–C(1)–N(3) | 122(2) |
| S(1)–Bi–S(3) | 84.2(3) | S(2)–C(10)–N(4) | 121(2) |
| S(2)–Bi–S(3) | 81.0(3) | S(2)–C(10)–N(6) | 126(2) |
| Bi–S(1)–C(1) | 104(1) | N(4)–C(10)–N(6) | 112(3) |
| Bi–S(2)–C(10) | 100(1) | S(3)–C(19)–N(7) | 119(2) |
| Bi–S(3)–C(19) | 107(1) | S(3)–C(19)–N(9) | 122(2) |
| S(1)–C(1)–N(1) | 114(2) | N(7)–C(19)–N(9) | 119(2) |
| S(1)–C(1)–N(3) | 124(2) | | |

symmetry at the origin of the cell, is co-ordinated by six sulphur atoms from the ligand molecules in a distorted octahedral environment. The co-ordination polyhedron is comparable with the $[Bi(tu)_6]^{3+}$ cation found in the ' red compound ',[2] in which the bismuth atom is located on a $\bar{3}$ inversion axis and is co-ordinated by six thiourea molecules through their sulphur atoms in an environment showing only a small distortion from octahedral geometry. Here, too, apart from the allyl groups, the cation approximates to $\bar{3}$ symmetry. The larger distortion

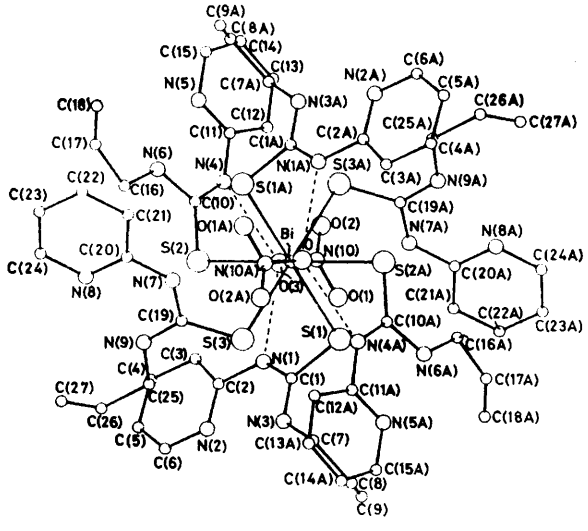


FIGURE 2 Projection of the structure of (2) along a pseudo-trigonal axis (excluding the disordered $NO_3^-$ ion)

observed in the nitrate derivative can be attributed to steric effects involving the bulky aptu molecules. The Bi–S bond distances (Table 5) show no significant variations and are similar to those found in the ' red compound ' and in other related S–Bi complexes.[1,2,11,12] In view of the rather high estimated standard deviations, the differences between the bond distances and angles in the three crystallographically independent ligand molecules are not significant, and the same can be said for the comparison with those found in (1). The structural parameters involving the terminal allyl carbons and the nitrate groups are less reliable owing to the large thermal motion (or disorder) affecting these atoms. As observed in (1), the thiourea and pyridine groups are planar and almost coplanar in each aptu molecule, the dihedral angles formed by their mean planes being 3.2, 3.2, and 2.9°. Again the ligand molecules are arranged so that the pyridine nitrogen atoms can form intramolecular hydrogen bonds.* N(11) is located on the symmetry

| | |
|---|---|
| N(3) · · · N(2) = 2.63(3) Å | N(3)–H · · · N(2) = 131° |
| N(6) · · · N(5) = 2.61(4) Å | N(6)–H · · · N(5) = 128° |
| N(9) · · · N(8) = 2.61(3) Å | N(9)–H · · · N(8) = 132° |

centre at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ and consequently its oxygen atoms have a disordered distribution in two centrosymmetric positions with a 0.5 population parameter. Refinement in the $P\bar{1}$ space group was unsuccessful, and led to unacceptable thermal parameters and worse values for bond distances and for the $R$ index.

Packing is determined by van der Waals contacts [Table 4(*b*)], some of them * being interpretable as hydrogen bonds.

| | |
|---|---|
| N(1) · · · O(3) = 2.95(5) Å | N(1)–H · · · O(3) = 167° |
| N(4) · · · O(3) = 2.88(4) Å | N(4)–H · · · O(3) = 168° |

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* See footnote on preceding page.

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