Synthesis and *X*-Ray Crystal Structure of Trichlorotris[1-phenyl-3-(2-pyridyl)-2-thiourea-*S*]bismuth(III) and Di-μ-chloro-tetrachloro-tetrakis(*NN'*-diethylimidazolidine-2-thione-*S*)dibismuth(III) †

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Two complexes of bismuth, $[BiCl_3(pptu)_3]$ (1) and $[\{BiCl_3(deimdt)_2\}_2]$ (2) [pptu = 1-phenyl-3-(2-pyridyl)-2-thiourea, deimdt = *NN'*-diethylimidazolidine-2-thione], have been synthesized and characterized by elemental analysis, i.r. spectra, and *X*-ray single-crystal structure determination. Compound (1) is triclinic, $a = 10.028(2)$, $b = 11.380(4)$, $c = 9.668(3)$ Å, $\alpha = 112.56(1)$, $\beta = 103.61(2)$, $\gamma = 95.22(2)°$, $Z = 1$, space group $P\bar{1}$; $R = 0.057$ for 2 876 'observed' data. The bismuth atom, at the origin of the cell, is octahedrally surrounded by two chlorines, two sulphurs from two ligand molecules and one sulphur from a further ligand molecule which is disordered with one chlorine with populations of 50%. Crystals of (2) are monoclinic, $a = 13.050(5)$, $b = 15.400(7)$, $c = 13.171(7)$ Å, $\beta = 117.99(1)°$, $Z = 2$, space group $P2_1/n$; $R = 0.051$ for 2 306 'observed' data. Co-ordination around bismuth is rather distorted octahedral involving two sulphurs from two ligands and four chlorines; two of them, more loosely bonded, bridge two adjacent co-ordinated polyhedra forming a dimeric complex molecule.

In previous work we have considered the structural properties of some complexes formed by $BiCl_3$ or $Bi(NO_3)_3$ and thiourea (tu) derivatives: $3BiCl_3\cdot7tu$ [1] and $BiCl_3\cdot3tu$ [2] contain two kinds of chemically non-equivalent bismuth atoms as octahedral cationic and anionic complexes, $[Bi_2Cl_4(tu)_6]^{2+}$ and $[BiCl_5(tu)]^{2-}$, and $[Bi(tu)_6]^{3+}$ and $[Bi\{(tu)_{1.5}Cl_{1.5}\}Cl_3]^{\frac{3}{2}-}$ respectively. Also, in $BiCl_3\cdot2imdt$ [3] (imdt = imidazolidine-2-thione), co-ordination of bismuth is octahedral but now two chloride ions bridge adjacent metal atoms so forming infinite zigzag chains. The structure of $3BiCl_3\cdot4tsc$ [3] (tsc = thiosemicarbazide) shows the presence of $[BiCl_6]^{3-}$ octahedral anions and tetrameric $[Bi_4Cl_{10}(tsc)_6]^{2+}$ cations where each of the three bismuth atoms in the $[\{BiCl_3(tsc)\}_3(\mu_3\text{-}Cl)]^-$ unit is distorted octahedral while in the remaining $[Bi(tsc)_3]^{3+}$ moiety it is trigonal antiprismatic. Octahedral geometry is observed also in $[\{BiCl_3(aptu)_2\}_2]$ and in $[Bi(aptu)_6][NO_3]_3$ [4] [aptu = 1-allyl-3-(2-pyridyl)-2-thiourea], the first being dimeric, the second containing discrete $[Bi(aptu)_6]^{3+}$ and NO_3^- ions. In continuing this research to study the interactions of the ligands with bismuth, we now report on the structures of $[BiCl_3(pptu)_3]$ (1) [pptu = 1-phenyl-3-(2-pyridyl)-2-thiourea] and $[\{BiCl_3(deimdt)_2\}_2]$ (2) (deimdt = *NN'*-diethylimidazolidine-2-thione).

Experimental

Complex (1) was obtained by reacting $BiCl_3$ with an excess of pptu in $CHCl_3$–MeCN (1 : 1). Complex (2) was formed by mixing $BiCl_3$ and deimdt in a 1 : 3 molar ratio in $CHCl_3$; after some days pale yellow prisms were grown. Elemental analyses: for (1) (Found: C, 42.5; H, 3.3; Bi, 20.5; Cl, 10.1; N, 11.8; S, 9.7. Calc. for $C_{36}H_{33}BiCl_3N_9S_3$: C, 43.1; H, 3.3; Bi, 20.8; Cl, 10.6; N, 12.5; S, 9.5%); for (2) (Found: C, 25.8; H, 4.3; Bi, 32.3; Cl, 17.0; N, 8.7; S, 10.3. Calc. for $C_{28}H_{56}Bi_2Cl_6N_8S_4$: C, 26.6; H, 4.5; Bi, 33.1; Cl, 16.8; N, 8.9; S, 10.2%). Main i.r. bands (cm^{-1}): for (1), 3 220s, 3 170s, 1 620 (sh), 1 600s, 1 550s, 1 530s, 1 495m, 1 480s, 1 430s, and 720w; for (2), 2 970m, 2 930m, 2 880m, 1 540vs, 1 495s, 1 455s, 1 430s, 1 380m, 1 350m, 1 335s, 1 280s, 1 200m, 1 130m, 1 080m, 960m, and 785m.

The ligands were synthesized following the methods in refs. 5 and 6 for pptu and deimdt respectively; i.r. spectra of the complexes were recorded by KBr discs on a Perkin-Elmer 283 B spectrophotometer.

Crystal Data.—Complex (1). $C_{36}H_{33}BiCl_3N_9S_3$, M = 1 003.3, Triclinic, $a = 10.028(2)$, $b = 11.380(4)$, $c = 9.668(3)$ Å, $\alpha = 112.56(1)$, $\beta = 103.61(2)$, $\gamma = 95.22(2)°$, $U = 970(2)$ Å^3, $D_m = 1.71$ g cm^{-3}, $Z = 1$, $D_c = 1.71$ g cm^{-3}, $F(000) = 494$, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 49.3 cm^{-1}, space group $P\bar{1}$ (from structural analysis).

Complex (2). $C_{28}H_{56}Bi_2Cl_6N_8S_4$, M = 1 263.7, Monoclinic, $a = 13.050(5)$, $b = 15.400(7)$, $c = 13.171(7)$ Å, $\beta = 117.99(1)°$, U = 2 337(2) Å^3, $D_m = 1.77$ g cm^{-3}, $Z = 2$, $D_c = 1.79$ g cm^{-3}, $F(000)$ = 1 224, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 80.4 cm^{-1}, space group $P2_1/n$ (from systematic absences).

Cell dimensions were refined using the θ values of 15 reflections, accurately measured on the diffractometer, by least-squares procedures.

Data Collection.—Three-dimensional intensity data were collected using an automated Siemens AED single-crystal diffractometer with niobium-filtered Mo-K_α radiation and ω—2θ scan technique. Crystals of dimensions 0.076 × 0.130 × 0.392 mm and 0.16 × 0.23 × 0.39 mm were used for (1) and (2) respectively: totals of 4 476 and 4 332 reflections were measured in the range $6 < 2\theta < 54°$ for (1) and $6 < 2\theta < 50°$ for (2) respectively; 2 876 and 2 306 unique 'observed' reflections having $I > 2\sigma(I)$ were used in the analyses. In both cases the intensity of a standard reflection was checked every 50 reflections; no significant change during data collection was observed.

The structure amplitudes were corrected for Lorentz and polarization effects and put on absolute scale by a least-squares method. Correction for absorption was applied only

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† *Supplementary data available* (No. SUP 23691, 34 pp.): thermal parameters, observed and calculated structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Final fractional atomic co-ordinates (× 10^4) with e.s.d.s for (1)

Atom	*x*	*y*	*z*
Bi	0	0	0
Cl(1)	1 585(5)	1 587(4)	2 905(5)
Cl, S	1 069(5)	1 631(6)	−1 204(6)
S(1)	2 158(4)	−1 480(4)	−449(4)
N(1)	2 662(11)	−1 044(11)	2 539(12)
N(2)	3 585(11)	−2 671(11)	1 084(13)
N(3)	4 002(9)	−1 886(9)	4 112(10)
N(4)	220(21)	4 076(22)	−713(28)
N(5)	1 222(22)	3 701(23)	1 387(25)
C(1)	2 864(13)	−1 768(13)	1 145(15)
C(2)	3 215(12)	−1 038(12)	4 021(14)
C(3)	4 547(17)	−1 832(17)	5 581(18)
C(4)	4 287(18)	−962(18)	6 872(17)
C(5)	3 441(17)	−119(16)	6 709(16)
C(6)	2 876(15)	−143(15)	5 258(16)
C(7)	3 941(14)	−3 466(13)	−278(14)
C(8)	4 942(19)	−2 943(18)	−747(19)
C(9)	5 342(25)	−3 700(24)	−2 009(22)
C(10)	4 803(25)	−4 904(25)	−2 758(23)
C(11)	3 798(27)	−5 542(18)	−2 390(25)
C(12)	3 325(19)	−4 766(18)	−1 027(21)
C(13)	784(27)	3 249(25)	−201(33)
C(14)	−445(15)	4 167(17)	−2 226(16)
C(15)	−300(19)	3 125(18)	−3 513(23)
C(16)	−851(18)	3 052(16)	−4 990(19)
C(17)	−1 496(17)	3 956(16)	−5 229(18)
C(18)	−1 627(19)	5 002(16)	−3 969(22)
C, N	−1 078(16)	5 048(13)	−2 503(19)

Table 2. Final fractional atomic co-ordinates (× 10^5 for Bi, × 10^4 for other atoms) with e.s.d.s for (2)

Atom	*x*	*y*	*z*
Bi	−45 073(5)	53 938(4)	36 637(5)
Cl(1)	−5 484(5)	6 400(3)	1 922(4)
Cl(2)	−5 192(5)	4 019(3)	2 349(5)
Cl(3)	−3 593(4)	4 506(4)	5 891(5)
S(1)	−2 445(4)	5 344(3)	3 524(4)
S(2)	−3 493(4)	7 035(3)	4 667(4)
N(1)	−2 373(14)	3 610(10)	3 145(14)
N(2)	−2 966(13)	4 434(11)	1 607(14)
N(3)	−3 247(13)	7 371(11)	6 768(12)
N(4)	−1 843(13)	6 552(10)	6 811(12)
C(1)	−2 592(15)	4 421(13)	2 722(15)
C(2)	−2 093(19)	3 340(14)	4 330(18)
C(3)	−850(22)	2 956(19)	4 929(23)
C(4)	−2 685(21)	2 957(15)	2 203(18)
C(5)	−2 992(23)	3 525(13)	1 172(19)
C(6)	−3 321(20)	5 184(12)	837(19)
C(7)	−2 345(23)	5 539(18)	656(27)
C(8)	−2 852(17)	6 988(12)	6 105(15)
C(9)	−4 322(19)	7 919(21)	6 305(20)
C(10)	−4 096(25)	8 831(17)	6 058(27)
C(11)	−2 461(20)	7 313(15)	8 014(19)
C(12)	−1 522(18)	6 643(15)	8 045(17)
C(13)	−1 082(26)	6 211(22)	6 429(26)
C(14)	−474(28)	5 439(21)	6 857(32)

to the data of (1), with transmission factors in the range 0.53—0.72.

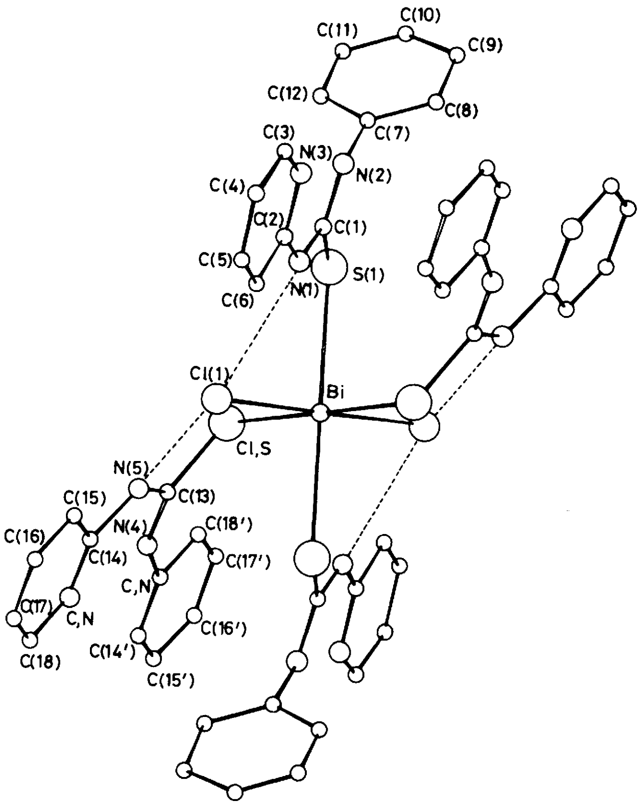

Figure 1. Projection of (1) along [0 0 1]; broken lines indicate hydrogen bonds

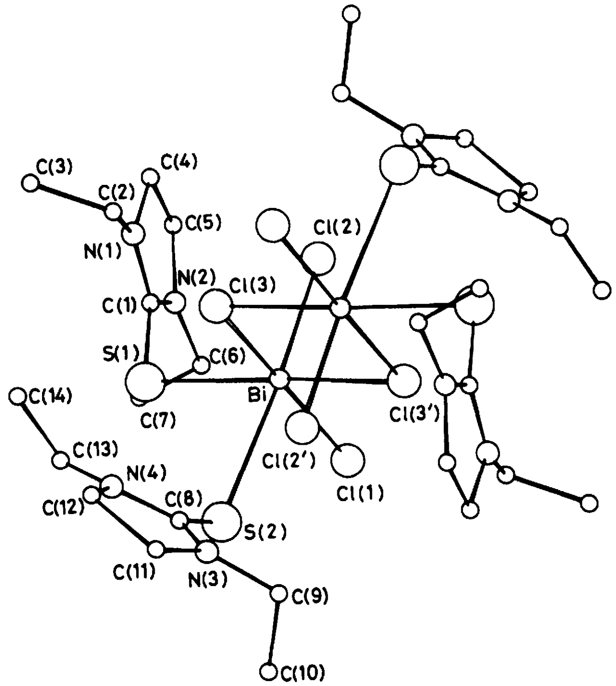

Figure 2. Projection of (2) along [0 0 1]

Structure Analysis.—In both cases the structures were solved by Patterson and Fourier methods; the Fourier phased by the heavy-atom contribution gave all the non-hydrogen atoms. The refinements were carried out first by isotropic and then anisotropic (for Bi, Cl, and S) cycles of full-matrix least-squares refinement. In (1), one pptu ligand and one chlorine were disordered and were refined with population parameters of 50%, and Cl and S were constrained to occupy the same position. The final values of *R* and *R′* were 0.057 and 0.061

Table 3. Bond distances (Å) and angles (°) in (1)

(*a*) Distances

Bi–Cl(1)	2.675(2)	N(3)–C(3)	1.37(1)	C(9)–C(10)	1.27(1)	C(14)–C(15)	1.40(1)
Bi–Cl, S	2.800(3)	C(3)–C(4)	1.36(1)	C(10)–C(11)	1.37(1)	C(15)–C(16)	1.37(1)
Bi–S(1)	2.872(2)	C(4)–C(5)	1.36(1)	C(11)–C(12)	1.48(1)	C(16)–C(17)	1.32(1)
S(1)–C(1)	1.70(1)	C(5)–C(6)	1.37(1)	C(12)–C(7)	1.37(1)	C(17)–C(18)	1.38(1)
C(1)–N(1)	1.35(1)	C(6)–C(2)	1.37(1)	S(2)–C(13)	1.80(1)	C(18)–C, N	1.37(1)
C(1)–N(2)	1.30(1)	N(2)–C(7)	1.42(1)	C(13)–N(4)	1.33(1)	C, N–C(14)	1.31(1)
N(1)–C(2)	1.40(1)	C(7)–C(8)	1.37(1)	C(13)–N(5)	1.36(1)	N(5)–C, N^{i}	1.46(1)
C(2)–N(3)	1.31(1)	C(8)–C(9)	1.37(1)	N(4)–C(14)	1.50(1)		

(*b*) Angles

Cl(1)–Bi–Cl, S	91.0(1)	N(3)–C(3)–C(4)	122(1)	S(2)–C(13)–N(4)	132(2)
Cl(1)–Bi–S(1)	90.6(1)	C(3)–C(4)–C(5)	119(1)	S(2)–C(13)–N(5)	113(2)
Cl, S–Bi–S(1)	91.7(1)	C(4)–C(5)–C(6)	120(1)	N(4)–C(13)–N(5)	114(2)
Bi–S(1)–C(1)	111.8(2)	C(5)–C(6)–C(2)	116(1)	N(4)–C(14)–C(15)	111(1)
Bi–S(2)–C(13)	109.2(4)	C(1)–N(2)–C(7)	124(1)	N(4)–C(14)–C, N	131(1)
S(1)–C(1)–N(1)	119(1)	N(2)–C(7)–C(8)	119(1)	C, N–C(14)–C(15)	117(1)
S(1)–C(1)–N(2)	122(1)	C(7)–C(8)–C(9)	120(1)	C(14)–C(15)–C(16)	119(1)
N(1)–C(1)–N(2)	118(1)	C(8)–C(9)–C(10)	120(2)	C(15)–C(16)–C(17)	121(1)
C(1)–N(1)–C(2)	129(1)	C(9)–C(10)–C(11)	123(2)	C(16)–C(17)–C(18)	120(1)
N(1)–C(2)–C(6)	116(1)	C(10)–C(11)–C(12)	117(2)	C(17)–C(18)–C, N	117(1)
N(1)–C(2)–N(3)	118(1)	C(11)–C(12)–C(7)	115(1)	C(14)–C, N–C(18)	124(1)
N(3)–C(2)–C(6)	125(1)	C(12)–C(7)–C(8)	121(1)	C(13)–N(5)–C, N	126(2)
C(2)–N(3)–C(3)	115(1)	C(12)–C(7)–N(2)	119(2)		

(*c*) Contacts less than 3.60 Å

N(4) ··· $C(12^{ii})$	3.39(3)	N(1) ··· $C(4^{iv})$	3.43(2)	C(4) ··· $C(1^{iv})$	3.56(2)
N(5) ··· $C(9^{iii})$	3.35(3)	N(3) ··· $C(6^{iv})$	3.49(1)		

i $\bar{x}, 1 - y, \bar{z}$; ii $x, y - 1, z$; iii $1 - x, \bar{y}, \bar{z}$; iv $1 - x, \bar{y}, 1 - z$.

for (1), and 0.051 and 0.052 for (2).* Two reflections for (1) and seven for (2) were excluded from the final refinement, probably being affected by counting error or extinction. The effects of anomalous dispersion were included in all structure factor calculations; the function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)$, with $w = 1/[\sigma^2(F_o) + gF_o^2]$; $g = 3.73 \times 10^{-2}$ for (1) and 6.66×10^{-3} for (2).

No attempts were made to locate the hydrogen atoms in either structure. Tables 1 and 2 contain the positional parameters with their e.s.d.s for (1) and (2) respectively. Atomic scattering factors were taken from International Tables,[7] the calculations were performed on the CYBER 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord Orientale Bologna, using the SHELX system of programs,[8] with financial support of the University of Parma.

Discussion

In (1) (Figure 1) the bismuth atom, on the symmetry centre at the origin, is surrounded by two chlorine atoms, two sulphurs from two ligand molecules, and by one chlorine atom and one ligand (*via* sulphur) which are both disordered with population factors of 50%. These disordered distributions between chlorine and sulphur atoms of thiourea molecules are not surprising; in the $[BiCl_5(tu)]^{2-}$ anion present in $3BiCl_3\cdot7tu$, the bismuth, occupying a symmetry centre, is co-ordinated by four chlorine atoms and one chlorine and one sulphur disordered atoms; in $BiCl_3\cdot3tu$ the anion $[Bi\{(tu)_{1.5}Cl_{1.5}\}Cl_3]^{3-}_{2}$ also shows the presence of three chlorine and three thiourea sulphur disordered atoms.

The co-ordination polyhedron can be described as a distorted octahedron with angles at bismuth close to 90° and co-ordination distances (Table 3) in the range quoted in the literature for similar compounds: Bi–Cl 2.529(8)—2.87(3), Bi–S 2.600(10)—2.886(6) Å, in $3BiCl_3\cdot7tu$ [1] and $BiCl_3\cdot3tu$; [2] Bi–S 2.611(5)—2.860(5) Å in $[Bi(S_2CNEt_2)_2X]$ (X = I or Br).[9] Octahedral co-ordination appears to be preferred by bismuth in complexes with monodentate ligands, *e.g.* in *NN'*-diethylthiocarbamoylpyridinium pentachloro(pyridine)bismuthate(III),[10] in 2-methylpyridinium tetrabromo- and tetraiodobismuthate(III),[11] and in caesium and tetraphenylphosphonium enneabromodibismuthate(III).[12]

The two independent ligand molecules in (1) show different arrangements: the dihedral angle between the mean planes of pyridine and the phenyl rings is 77.7° in the molecule containing S(1), and 0° in that containing S(2), as in the latter the phenyl and pyridine rings are correlated by a symmetry centre at $0\,\tfrac{1}{2}\,0$, so that N(6) and C(19) have a further disordered distribution with a population parameter of 50% (C,N). Thiourea moieties and pyridine rings in both molecules are planar and roughly coplanar: dihedral angle between the planes S(1),C(1),N(1),N(2) and C(2)—C(6),N(3) = 5°; S(2),C(13),N(4),N(5) and C(14)—C(18),N(6) = 8°; in the first molecule they are arranged so that pyridine and thiourea nitrogen atoms can form an intramolecular hydrogen bond [N(2) ··· N(3) 2.62(1) Å].

The structural parameters of these molecules are normal, but the C(13)–N(4)–C(14) and N(4)–C(14)–N(6) angles of 140(2) and 131(1)° respectively are significantly larger than the corresponding ones, which range from 124(1) to 129(1)° in the first, and are near to 120(1)° in the latter. These discrepancies are justified considering the greater steric hindrance between the two rings which are coplanar. The packing in the structure is determined from van der Waals contacts and by possible

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* Attempts to refine the structure of (1) in the $P1$ space group gave higher R,R' indices and unacceptable structural parameters.

Table 4. Bond distances (Å) and angles (°) for (2)

(*a*) Distances

Bi–Cl(1)	2.558(4)	S(1)–C(1)	1.72(1)	C(2)–C(3)	1.54(3)	N(4)–C(8)	1.37(2)
Bi–Cl(2)	2.613(5)	N(1)–C(1)	1.34(2)	C(4)–C(5)	1.50(3)	N(4)–C(12)	1.48(2)
Bi–Cl(3)	2.934(5)	N(1)–C(2)	1.48(2)	C(6)–C(7)	1.50(4)	N(4)–C(13)	1.40(4)
Bi–S(1)	2.783(5)	N(1)–C(4)	1.49(2)	S(2)–C(8)	1.67(1)	C(9)–C(10)	1.50(4)
Bi–S(2)	2.871(4)	N(2)–C(1)	1.31(2)	N(3)–C(8)	1.34(2)	C(11)–C(12)	1.58(3)
Bi–Cl(3^{i})	2.807(6)	N(2)–C(5)	1.50(2)	N(3)–C(9)	1.49(2)	C(13)–C(14)	1.39(5)
Bi · · · Bi	4.446(2)	N(2)–C(6)	1.46(2)	N(3)–C(11)	1.47(2)		

(*b*) Angles

Cl(1)–Bi–Cl(2)	91.4(2)	Bi–S(1)–C(1)	103.3(6)	Bi–S(2)–C(8)	111.1(6)
Cl(1)–Bi–Cl(3)	167.5(2)	S(1)–C(1)–N(1)	124(1)	S(2)–C(8)–N(4)	126(1)
Cl(1)–Bi–Cl(3^{i})	92.1(2)	S(1)–C(1)–N(2)	123(1)	S(2)–C(8)–N(3)	125(1)
Cl(1)–Bi–S(1)	92.7(2)	N(1)–C(1)–N(2)	111(1)	N(3)–C(8)–N(4)	108(1)
Cl(1)–Bi–S(2)	78.9(2)	C(1)–N(1)–C(4)	111(1)	C(8)–N(3)–C(11)	114(1)
Cl(2)–Bi–Cl(3)	97.8(3)	C(1)–N(1)–C(2)	126(1)	C(8)–N(3)–C(9)	123(1)
Cl(2)–Bi–Cl(3^{i})	97.0(2)	C(2)–N(1)–C(4)	121(1)	C(9)–N(3)–C(11)	121(1)
Cl(2)–Bi–S(1)	88.5(2)	N(1)–C(2)–C(3)	108(1)	N(3)–C(9)–C(10)	111(2)
Cl(2)–Bi–S(2)	163.4(2)	N(1)–C(4)–C(5)	102(1)	N(3)–C(11)–C(12)	101(1)
Cl(3)–Bi–Cl(3^{i})	78.5(2)	N(2)–C(5)–C(4)	104(1)	N(4)–C(12)–C(11)	102(1)
Cl(3)–Bi–S(1)	95.8(2)	C(1)–N(2)–C(5)	109(1)	C(8)–N(4)–C(12)	112(1)
Cl(3)–Bi–S(2)	93.8(2)	C(1)–N(2)–C(6)	128(1)	C(8)–N(4)–C(13)	123(1)
Cl(3^{i})–Bi–S(1)	172.5(2)	C(5)–N(2)–C(6)	121(1)	C(12)–N(4)–C(13)	122(1)
Cl(3^{i})–Bi–S(2)	96.7(2)	N(2)–C(6)–C(7)	112(1)	N(4)–C(13)–C(14)	122(2)
S(1)–Bi–S(2)	78.6(2)				

(*c*) Intermolecular contacts less than 3.60 Å

Cl(1) · · · N(4^{ii})	3.58(1)	C(5) · · · S(2^{iii})	3.50(2)	Cl(2) · · · N(3^{iv})	3.50(2)	Cl(2) · · · C(11^{iv})	3.52(2)

i $-1 - x, 1 - y, 1 - z$; ii $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$; iii $-\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; iv $-1 - x, 1 - y, 1 - z$.

hydrogen bonds involving the Cl(1) atom [Cl(1) · · · N(1) 3.19(1), Cl(1) · · · N(5) 3.27(3) Å].

The structure of [{BiCl$_3$(deimdt)$_2$}$_2$] (2) shows several features similar to that found in [BiCl$_3$(pptu)$_3$] (1): the coordination around the bismuth is rather distorted octahedral [the *cis* angles are in the range 78.5(2)—97.8(3)°, Table 4] involving four chlorines and two sulphur atoms of two ligand molecules located on two adjacent positions of the octahedron. Two chlorines are more strictly bonded [Bi–Cl(1) 2.558(4), Bi–Cl(2) 2.613(5) Å]; the two remaining, related by a symmetry centre, bridge asymmetrically two adjacent polyhedra [Bi–Cl (3^{i}) 2.807(6), Bi–Cl(3) 2.934(5) Å] which share an edge forming a dimeric complex molecule. Also in this case, as shown in the pptu complex, the longer Bi–Cl (bridge) bond distance is opposite in the octahedron to the shorter Bi–Cl(1) distance and the Bi–S(2) bond distance of 2.871(4) Å, which is approximately normal to the bridge plane, is significantly longer than the Bi–S(1) bond [2.783(5) Å]. These Bi–S bonds show values comparable with those generally found in the literature for these complexes;[9] the two Bi–Cl terminal bonds have the shorter values in agreement with the fact, that in this structure, these chlorines cannot show hydrogen bonds or short intramolecular contacts.

Bond distances and angles in the two independent ligand molecules are in the usual range, excepting those involving C(13) and C(14), which are affected by higher thermal motion or disorder. The thiourea moieties are planar and their mean planes form a dihedral angle of 49.7°. The discrete dimeric units are joined by van der Waals contacts (Table 4).

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