

Synthesis, Characterization, and Crystal Structure of μ -[1'-Pyrrolidine-carbodithioato-S(Bi¹⁻²)S'(Bi²)]-1,1,1,2,2-pentakis(1'-pyrrolidinecarbodithioato-SS')dibismuth(III) Ethanol (1/1) and of Di- μ -chloro-bis[bis(1'-pyrrolidinecarbodithioato-SS')(thiourea-S)bismuth(III)][†]

Luigi P. Battaglia* and Anna Bonamartini Corradi

Istituto di Chimica Generale ed Inorganica Centro di Studio per la Strutturistica Diffraattometrica del C.N.R., Via Massimo D'Azeglio, 85-43100 Parma, Italy

Reaction of BiCl₃ and ammonium 1-pyrrolidinecarbodithioate, [NH₄]pcdt, in CH₂Cl₂-EtOH (1:1) gave [$\{\text{Bi}(\text{pcdt})_3\}_2$]-EtOH (1). Grinding BiCl₃ and thiourea (tu) and reacting with [NH₄]pcdt in CH₂Cl₂-EtOH (1:1) gave [$\{\text{Bi}(\text{tu})(\text{pcdt})_2\text{Cl}\}_2$] (2). Compounds (1) and (2) have been characterized by single-crystal X-ray diffraction: both are triclinic, space group *P* $\bar{1}$, with for (1), *a* = 15.907(7), *b* = 14.429(7), *c* = 11.253(6) Å, α = 82.84(8), β = 84.55(9), γ = 81.02(9)°, *Z* = 2 and *R* = 0.065. For (2), *a* = 10.491(6), *b* = 11.335(8), *c* = 8.812(7) Å, α = 102.58(8), β = 107.44(6), γ = 97.44(8)°, *Z* = 1, and *R* = 0.028. In (1) the co-ordination around one bismuth atom is trigonal prismatic with an extraposition on a rectangular face, and pentagonal pyramidal around the other bismuth atom; a sulphur atom joins the two polyhedra with an asymmetric bridge. In (2) co-ordination at bismuth is pentagonal bipyramidal; two chlorines, one apical and one equatorial, are bridging so that two adjacent polyhedra share an edge.

We have previously considered the structural properties of some bismuth complexes with thiourea and thiourea derivatives,¹⁻⁴ in which it was found that co-ordination occurs invariably *via* sulphur atoms and, with unidentate ligands, the octahedral geometry is preferred, the influence of the lone pair never being observed. In this paper we report the results of a study on the crystal structures of [$\{\text{Bi}(\text{pcdt})_3\}_2$]-EtOH (1) and [$\{\text{Bi}(\text{tu})(\text{pcdt})_2\text{Cl}\}_2$] (2) (pcdt = 1-pyrrolidinecarbodithioate, tu = thiourea) in which the presence of the bidentate ligands produces trigonal prismatic, pentagonal pyramidal, and pentagonal bipyramidal geometries around bismuth.

Experimental

Compound (1) was prepared by reaction of BiCl₃ and [NH₄]pcdt (1:3) in CH₂Cl₂-tetrahydrofuran (thf) (1:1). Recrystallization from CH₂Cl₂-EtOH (1:1) gave yellow plates. Complex (2) was synthesized by grinding BiCl₃ and thiourea (1:3) and dissolving in CH₂Cl₂-EtOH (1:1) in the presence of an excess of [NH₄]pcdt. After several days gold-yellow prisms were formed. Yields: 95% for (1), very low for (2). Elemental analyses gave the following results. Found for (1): C, 29.2; H, 3.9; Bi, 32.0; N, 6.2; S, 28.1. Calc. for C₃₂H₅₄Bi₂N₆OS₁₂: C, 28.7; H, 4.1; Bi, 31.2; N, 6.3; S, 28.7%. Found for (2): C, 21.8; H, 3.4; Bi, 34.8; N, 9.8; S, 26.5. Calc. for C₂₂H₄₀Bi₂Cl₂N₈S₁₀: C, 21.6; H, 3.3; Bi, 34.1; N, 9.1; S, 26.2%. The i.r. frequencies (cm⁻¹), obtained using KBr discs and a Perkin-Elmer 283 B spectrophotometer, are as follows. For (1) 1 510m, 1 430vs, br, 1 330s, 1 240s, 1 215s, 1 160s, 1 000s, 940s, 910s, 825s, 755m, 695m; for (2) 1 600vs, 1 480vs, 1 440vs, 1 400vs, 1 330s, 1 245m, 1 210m, 1 175m, 1 155m, 1 100w, 1 040w, 990w, 940s, 910m, 855w, 820w, 825s, 690w.

Cell parameters were obtained by single-crystal diffractometry using Mo-K α radiation (λ = 0.710 69 Å) and the final accurate values were determined by least-squares refinement. Table 1 reports the relevant crystal and diffraction

data. The intensity data were collected on a Philips PW 1100 automated diffractometer and in both cases a standard reflection was remeasured after 60 min; the greatest variations observed were 9 and 2% of the initial values respectively for (1) and (2); the data were corrected for decay and Lorentz and polarization effects; an empirical absorption correction was also applied.⁵ The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares using isotropic and anisotropic thermal parameters for the Bi, Cl, and S atoms. The final *R* values were 0.065 and 0.028 for (1) and (2) respectively. The hydrogen atoms in (1) were not located, while in (2) the co-ordinates of these atoms, deduced from a ΔF map, were introduced in the last cycle as fixed contributors; 11 reflections, which appeared to be affected by extinction or counting errors, were suppressed at this stage. Tables 2 and 3 give the final atomic co-ordinates. Scattering factors, with corrections for anomalous dispersion, were taken from International Tables.⁶ All calculations were performed using the SHELX-76⁷ system of programs on the CYBER 76 computer of the Consorzio per la gestione del Centro di Calcolo Elettronico Inter-universitario dell'Italia Nord-Orientale (Bologna) with financial support from the University of Parma.

Discussion

In the structure of (1) (Figure 1) the unit cell contains two dinuclear units in which the two co-ordination polyhedra are different. The geometry around Bi(1) can be described as a distorted trigonal prism [Figure 2(a)] with S(3), S(4), S(9) and S(2), S(5), S(6) at the triangular bases [dihedral angle between their mean planes 10.5(3)°]; the S(1) atom occupies an extraposition on the S(5), S(3), S(9), S(2) rectangular face. The Bi(2) atom can be considered to be approximately at the centre of the base of a very distorted pentagonal pyramid [Figure 2(b)], the base being formed by S(7), S(10), S(9), S(12), S(8) and at the apex S(11). At the opposite side to S(11), Bi(2) exerts only two weak interactions [Bi(2)-S(1) 3.415(6) and Bi(2)-S(3) 3.427(7) Å] and in this direction the sterically active lone pair can be localized. The weak interactions, together with the Bi(1)-S(9) long bond distance [3.163(6) Å], join the two

[†] Supplementary data available (No. SUP 56507, 6 pp.); thermal parameters, non-bonding contacts, torsion angles, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii-xx. Structure factors are available from the editorial office.

Table 1. Experimental data for the crystallographic analyses of $[\{\text{Bi}(\text{pcdt})_3\}_2]\cdot\text{EtOH}$ (1) and $[\{\text{Bi}(\text{tu})(\text{pcdt})_2\text{Cl}\}_2]$ (2)

Compound	(1)	(2)
Formula	$\text{C}_{32}\text{H}_{54}\text{Bi}_2\text{N}_6\text{OS}_{12}$	$\text{C}_{22}\text{H}_{40}\text{Bi}_2\text{Cl}_2\text{N}_8\text{S}_{10}$
<i>M</i>	1 341.50	1 226.08
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> /Å	15.907(7)	10.491(6)
<i>b</i> /Å	14.429(7)	11.335(8)
<i>c</i> /Å	11.253(6)	8.812(7)
α /°	82.84(8)	102.58(8)
β /°	84.55(9)	107.44(6)
γ /°	81.02(9)	97.44(8)
<i>Z</i>	2	1
<i>U</i> /Å ³	2 524(2)	954(1)
<i>D_c</i> /g cm ⁻³	1.765	2.134
<i>D_m</i> /g cm ⁻³	1.74	2.10
Reflections for lattice parameters	{ number θ range/°	{ number θ range/°
<i>F</i> (000)	1 308	588
<i>T</i> /K	293	293
Crystal size/mm	0.16 × 0.29 × 0.55	0.20 × 0.29 × 0.49
μ /cm ⁻¹	74.5	98.8
Absorption correction (min., max.)	1.00, 2.27	1.00, 1.42
Scan speed/° s ⁻¹	0.10	0.10
Scan width	1.5 + 0.4 tan θ	1.3 + 0.3 tan θ
θ range/°	2.5—25	3—23
<i>h</i> range	± 18	± 10
<i>k</i> range	± 17	± 12
<i>l</i> range	0—11	0—9
Standard reflection	3 $\bar{4}$ 2	4 $\bar{1}$ 2
Intensity variation (% of initial value)	9	2
Scan mode	ω —2θ	ω —2θ
No. of measured reflections	7 950	2 636
Condition for observed reflections	$I > 3\sigma(I)$	$I > 3\sigma(I)$
No. of 'observed' independent reflections	4 889	2 317
Min., max. height in final ΔF map (e Å ⁻³)	-1.20, 2.05	-0.35, 0.28
No. of refined parameters	304	204
$R = \Sigma \Delta F /\Sigma F_o$	0.065	0.028
$R' = [\Sigma w(\Delta F^2)/\Sigma w F_o^2]^{1/2}$	0.069	0.029
$K, g A_w = K[\sigma^2(F) + g F_o^2]$	1.90, 1.4 × 10 ⁻³	1.23, 2.9 × 10 ⁻⁴

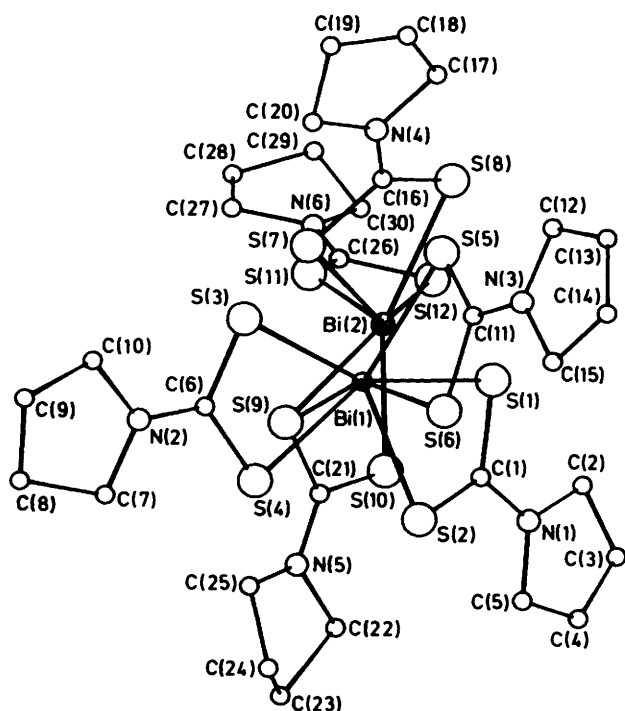
Table 2. Fractional atomic co-ordinates (× 10⁴) for $[\{\text{Bi}(\text{pcdt})_3\}_2]\cdot\text{EtOH}$ (1)

Atom	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>	Atom	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>
Bi(1)	2 662(0)	0(1)	3 168(1)	C(8)	2 245(20)	3 722(24)	-1 211(34)
Bi(2)	2 879(0)	2 719(1)	4 116(1)	C(9)	3 259(19)	3 585(21)	-1 258(30)
S(1)	3 789(4)	413(4)	4 609(6)	C(10)	3 429(15)	2 939(18)	-92(26)
S(2)	2 687(5)	-1 059(5)	5 497(7)	C(11)	3 132(13)	-1 992(15)	2 017(22)
S(3)	3 494(3)	1 355(4)	1 812(6)	C(12)	4 354(15)	-3 010(17)	1 130(25)
S(4)	1 795(5)	1 109(6)	1 055(7)	C(13)	4 369(24)	-3 955(26)	562(37)
S(5)	3 869(3)	-1 260(4)	2 277(6)	C(14)	3 499(21)	-3 982(23)	357(33)
S(6)	2 096(4)	-1 738(5)	2 508(9)	C(15)	2 882(19)	-3 425(21)	1 333(31)
S(7)	4 123(4)	3 015(5)	5 515(6)	C(16)	4 671(13)	3 475(14)	4 204(21)
S(8)	4 177(5)	3 741(7)	2 920(7)	C(17)	5 910(18)	4 139(21)	3 295(30)
S(9)	1 414(3)	1 652(4)	4 287(6)	C(18)	6 820(19)	4 160(21)	3 860(31)
S(10)	2 289(3)	2 010(4)	6 406(6)	C(19)	6 787(17)	3 795(19)	5 048(28)
S(11)	1 912(4)	4 243(4)	4 741(7)	C(20)	5 919(16)	3 441(18)	5 422(27)
S(12)	1 922(4)	3 869(5)	2 203(7)	C(21)	1 559(10)	1 514(12)	5 795(18)
N(1)	3 670(15)	-308(17)	6 824(25)	C(22)	1 142(16)	843(19)	7 866(27)
N(2)	2 679(11)	2 473(12)	118(18)	C(23)	549(30)	36(33)	8 263(48)
N(3)	3 440(13)	-2 754(14)	1 548(21)	C(24)	17(23)	-20(25)	7 375(38)
N(4)	5 429(11)	3 714(13)	4 308(19)	C(25)	419(15)	493(17)	6 149(25)
N(5)	1 083(11)	984(13)	6 558(19)	C(26)	1 590(14)	4 538(16)	3 284(23)
N(6)	1 051(12)	5 414(14)	3 102(20)	C(27)	773(18)	6 095(21)	4 004(30)
C(1)	3 401(16)	-291(18)	5 760(27)	C(28)	230(24)	6 905(27)	3 568(41)
C(2)	4 175(19)	397(22)	7 140(32)	C(29)	130(21)	6 708(24)	2 555(37)
C(3)	4 069(24)	270(30)	8 558(41)	C(30)	768(20)	5 747(23)	1 953(33)
C(4)	3 886(26)	-637(33)	8 918(43)	C(1A)	537(14)	7 000(16)	7 356(23)
C(5)	3 337(23)	-969(26)	7 934(38)	C(2A)*	714(24)	5 857(27)	7 176(41)
C(6)	2 641(13)	1 716(15)	918(22)	C(3A)*	503(23)	7 255(25)	8 797(40)
C(7)	1 961(17)	2 867(19)	-655(28)	O	1 045(9)	7 617(10)	6 491(15)

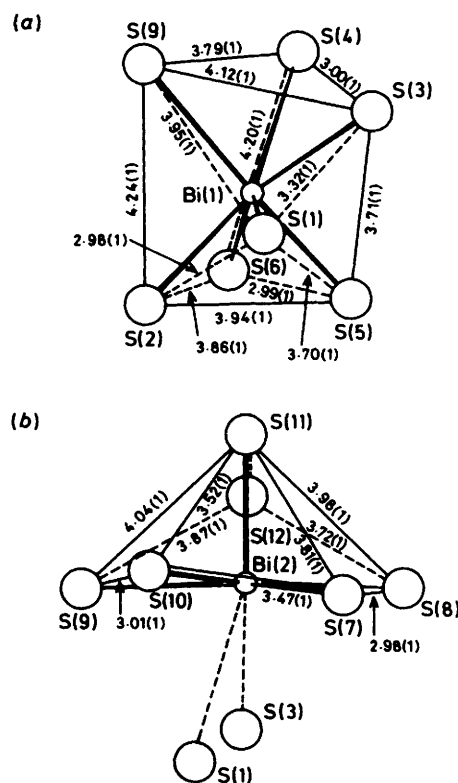
* Population parameter = 0.5.

Table 3. Fractional atomic co-ordinates ($\times 10^4$) for $[\{\text{Bi}(\text{tu})(\text{pcdt})_2\text{Cl}\}_2] (2)$

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Bi	1 789(0)	1 686(0)	1 220(0)	C(11)	2 765(9)	345(7)	5 159(10)
S(1)	2 699(2)	3 578(2)	3 859(3)	H(1)	213	6 054	1 893
S(2)	118(2)	3 428(2)	1 213(3)	H(2)	-777	5 492	2 993
S(3)	2 516(2)	3 060(2)	-580(3)	H(3)	-143	7 346	4 913
S(4)	4 403(2)	1 741(2)	1 220(3)	H(4)	747	7 938	3 733
S(5)	3 177(3)	219(3)	3 457(3)	H(5)	2 725	7 951	5 523
Cl	796(3)	318(2)	1 817(3)	H(6)	1 840	7 602	6 844
N(1)	1 288(7)	5 311(6)	3 804(8)	H(7)	2 187	5 641	6 395
N(2)	4 920(7)	2 964(6)	-794(8)	H(8)	3 322	6 090	5 394
N(3)	1 622(8)	624(7)	5 260(9)	H(9)	6 879	2 988	815
N(4)	3 637(8)	182(7)	6 495(10)	H(10)	6 175	1 656	-878
C(1)	1 359(8)	4 213(7)	3 008(10)	H(11)	7 512	2 730	-2 026
C(2)	232(9)	5 964(8)	3 133(11)	H(12)	7 504	4 180	-793
C(3)	647(13)	7 196(11)	4 366(15)	H(13)	5 945	4 148	-3 354
C(4)	1 890(15)	7 273(12)	5 596(18)	H(14)	5 314	2 542	-3 867
C(5)	2 266(10)	6 039(8)	5 407(11)	H(15)	3 592	3 247	-2 941
C(6)	4 058(8)	2 621(7)	-120(10)	H(16)	4 725	4 591	-1 515
C(7)	6 264(9)	2 655(8)	-493(11)	H(17)	969	753	4 282
C(8)	6 881(11)	3 275(9)	-1 521(13)	H(18)	1 366	698	6 236
C(9)	5 697(11)	3 391(10)	-2 834(13)	H(19)	4 495	-44	6 449
C(10)	4 638(9)	3 626(8)	-2 043(11)	H(20)	3 412	236	7 498

**Figure 1.** Projection of the dimer in (1)

polyhedra with a $\text{Bi}(1) \cdots \text{Bi}(2)$ interatomic distance of 4.264(3) Å. The Bi-S bond distances [Table 4(a)] fall in a wide range of values, 2.645(6)–3.163(6) Å for Bi(1) and 2.612(7)–2.966(6) Å for Bi(2), which compare well with those found in other bismuth–dithio complexes {e.g. in $[\text{Bi}(\text{S}_2\text{CNEt}_2)_3]$, 2.964(4)–2.595(8) Å;⁸ in $[\text{Bi}_3(\text{S}_2\text{CNEt}_2)_8\text{X}_7] \cdot \text{dmf}$ (X = Cl, Br, or I; dmf = dimethylformamide), 2.81(1)–2.60(1) Å⁹}. The extreme value of 3.163(6) Å involving S(9) is justified considering the bridging function of this atom. All the ligands are asymmetrically co-ordinated to a metal atom, a fact which is not unusual and can be related to the crowding of these

**Figure 2.** The co-ordinated polyhedra in the structure of (1): (a) Bi(1), (b) Bi(2)

molecules and with the rigidity of the CS_2 groups in which the sulphur atoms are fixed at near 3 Å [2.97(1)–3.01(1) Å] apart. This arrangement can minimize the repulsive interactions of the type $\text{S} \cdots \text{S}$; the maximum of these is reached around S(1) with the $\text{S}(1) \cdots \text{S}(3)$ contact 3.315(9) Å. The S-Bi-S angles for each pcdt molecule show characteristic expected values [62.3(3)–64.6(3)°], those involving the adjacent sulphur atoms are in the range 74.8(2)–91.3(2)° for Bi(1) and 77.5(2)–93.3(3)° for Bi(2),

Table 4. Selected bond distances (Å) and angles (°) *

(a) for (1)							
Bi(1)–S(1)	2.707(7)	Bi(2)–S(7)	2.757(8)	S(1)–C(1)	1.68(3)	S(7)–C(16)	1.75(2)
Bi(1)–S(2)	2.865(8)	Bi(2)–S(8)	2.860(9)	S(2)–C(1)	1.77(3)	S(8)–C(16)	1.68(2)
Bi(1)–S(3)	2.754(6)	Bi(2)–S(9)	2.966(6)	S(3)–C(6)	1.74(2)	S(9)–C(21)	1.72(2)
Bi(1)–S(4)	3.017(8)	Bi(2)–S(10)	2.784(7)	S(4)–C(6)	1.70(2)	S(10)–C(21)	1.69(2)
Bi(1)–S(5)	2.645(6)	Bi(2)–S(11)	2.612(7)	S(5)–C(11)	1.74(2)	S(11)–C(26)	1.75(3)
Bi(1)–S(6)	2.991(9)	Bi(2)–S(12)	2.941(8)	S(6)–C(11)	1.67(2)	S(12)–C(26)	1.64(3)
Bi(1)–S(9)	3.163(6)						
S(1)–Bi(1)–S(2)	64.6(3)	S(7)–Bi(2)–S(8)	63.9(3)	S(1)–C(1)–S(2)		120(2)	
S(1)–Bi(1)–S(3)	74.8(2)	S(7)–Bi(2)–S(9)	139.3(2)	S(1)–C(1)–N(1)		119(2)	
S(1)–Bi(1)–S(4)	132.6(3)	S(7)–Bi(2)–S(10)	77.5(2)	S(2)–C(1)–N(1)		121(2)	
S(1)–Bi(1)–S(5)	89.3(3)	S(7)–Bi(2)–S(11)	90.4(3)	S(3)–C(6)–S(4)		121(1)	
S(1)–Bi(1)–S(6)	137.1(3)	S(7)–Bi(2)–S(12)	134.7(3)	S(3)–C(6)–N(2)		118(2)	
S(1)–Bi(1)–S(9)	84.2(2)	S(8)–Bi(2)–S(9)	155.9(2)	S(4)–C(6)–N(2)		121(2)	
S(2)–Bi(1)–S(3)	139.3(3)	S(8)–Bi(2)–S(10)	141.0(3)	S(5)–C(11)–S(6)		122(1)	
S(2)–Bi(1)–S(4)	154.0(3)	S(8)–Bi(2)–S(11)	93.3(3)	S(5)–C(11)–N(3)		116(2)	
S(2)–Bi(1)–S(5)	91.3(2)	S(8)–Bi(2)–S(12)	79.8(3)	S(6)–C(11)–N(3)		122(2)	
S(2)–Bi(1)–S(6)	82.3(2)	S(9)–Bi(2)–S(10)	63.0(2)	S(7)–C(16)–S(8)		120(1)	
S(2)–Bi(1)–S(9)	89.3(2)	S(9)–Bi(2)–S(11)	92.7(3)	S(7)–C(16)–N(4)		117(2)	
S(3)–Bi(1)–S(4)	62.3(3)	S(9)–Bi(2)–S(12)	81.8(3)	S(8)–C(16)–N(4)		122(2)	
S(3)–Bi(1)–S(5)	86.7(2)	S(10)–Bi(2)–S(11)	81.2(2)	S(9)–C(21)–S(10)		124(1)	
S(3)–Bi(1)–S(6)	131.2(3)	S(10)–Bi(2)–S(12)	129.3(3)	S(9)–C(21)–N(5)		120(2)	
S(3)–Bi(1)–S(9)	88.0(2)	S(11)–Bi(2)–S(12)	64.4(3)	S(10)–C(21)–N(5)		116(2)	
S(4)–Bi(1)–S(5)	106.5(2)	Bi(1)–S(1)–C(1)	91(1)	S(11)–C(26)–S(12)		122(2)	
S(4)–Bi(1)–S(6)	88.7(3)	Bi(1)–S(2)–C(1)	84(1)	S(11)–C(26)–N(6)		115(2)	
S(4)–Bi(1)–S(9)	75.6(2)	Bi(1)–S(3)–C(6)	92(1)	S(12)–C(26)–N(6)		123(2)	
S(5)–Bi(1)–S(6)	63.7(3)	Bi(1)–S(4)–C(6)	84(1)	Bi(1)–S(9)–Bi(2)		88.1(2)	
S(5)–Bi(1)–S(9)	172.5(3)	Bi(1)–S(5)–C(11)	92(1)	Bi(2)–S(9)–C(21)		83(1)	
S(6)–Bi(1)–S(9)	123.8(3)	Bi(1)–S(6)–C(11)	82(1)	Bi(1)–S(9)–C(21)		106(1)	
		Bi(2)–S(7)–C(16)	88(1)	Bi(2)–S(10)–C(21)		88(1)	
		Bi(2)–S(8)–C(16)	86(1)	Bi(2)–S(11)–C(26)		91(1)	
				Bi(2)–S(12)–C(26)		82(1)	
(b) for (2)							
Bi–S(1)	2.624(4)	Bi–S(5)	3.017(4)	S(1)–C(1)	1.709(9)	S(3)–C(6)	1.712(9)
Bi–S(2)	2.805(3)	Bi–Cl	2.911(4)	S(2)–C(1)	1.686(7)	S(4)–C(6)	1.694(10)
Bi–S(3)	2.649(3)	Bi–Cl'	3.187(4)	S(5)–C(11)	1.66(1)		
Bi–S(4)	2.735(3)						
S(1)–Bi–S(2)	65.8(1)	S(3)–Bi–S(4)	65.9(1)	Bi–S(1)–C(1)		89.2(3)	
S(1)–Bi–S(3)	91.2(1)	S(3)–Bi–S(5)	135.9(2)	Bi–S(2)–C(1)		83.8(4)	
S(1)–Bi–S(4)	89.7(1)	S(3)–Bi–Cl	85.6(1)	Bi–S(3)–C(6)		88.8(3)	
S(1)–Bi–S(5)	86.0(1)	S(3)–Bi–Cl'	143.0(1)	Bi–S(4)–C(6)		86.4(5)	
S(1)–Bi–Cl	176.8(2)	S(4)–Bi–S(5)	70.0(1)	Bi–S(5)–C(11)		114.1(4)	
S(1)–Bi–Cl'	100.1(1)	S(4)–Bi–Cl	89.6(2)	S(2)–C(1)–N(1)		120.3(7)	
S(2)–Bi–S(3)	76.3(2)	S(4)–Bi–Cl'	148.1(2)	S(1)–C(1)–N(1)		118.8(7)	
S(2)–Bi–S(4)	134.4(2)	S(5)–Bi–Cl	96.7(1)	S(1)–C(1)–S(2)		120.9(6)	
S(2)–Bi–S(5)	139.2(1)	S(5)–Bi–Cl'	80.4(1)	S(4)–C(6)–N(2)		121.8(8)	
S(2)–Bi–Cl	112.7(1)	Cl–Bi–Cl'	82.1(1)	S(3)–C(6)–N(2)		119.5(8)	
S(2)–Bi–Cl'	76.6(2)			S(3)–C(6)–S(4)		119(1)	

* Primes indicate atom at \bar{x} , \bar{y} , \bar{z} .

while the remainder lie in the ranges 106.5(2)–154.0(3) and 129.3(3)–155.9(2)° for Bi(1) and Bi(2) respectively confirming the large deformation of the co-ordination polyhedra. The S–C bond distances [1.64(3)–1.77(3)Å] are normal and in agreement with those found in the literature for the uncomplexed¹⁰ and complexed ligand,^{11–13} their differences not being significant ($\Delta/\sigma = 3.06$). Also the $C(sp^2)$ –N, N– $C(sp^3)$, and $C(sp^3)$ – $C(sp^3)$ bond distances show the expected values and, in particular the C–C bond distances away from the S₂CN groups are always shorter than 1.54 Å due to partial disordering effects which affect these portions of the rings.¹⁰ The strain in the pentagonal rings is reflected in the angles at the carbons adjacent to the N atoms which as a result are generally less than the tetrahedral values. The S₂CN fragments are planar

and the deviations from these planes are significant for the bismuth atoms [0.162(3)–0.437(6) Å for Bi(1), 0.113(6)–0.439(5) Å for Bi(2)] in each polyhedron.

The puckering parameters¹⁴ of the pyrrolidine rings reveal different situations: the rings N(1)–C(5), N(2)–C(10), N(3)–C(15), and N(5)–C(25) are similar with 'twist' conformations (puckering parameters: $q_2 = 0.29, 0.32, 0.28, 0.18$ Å; $\varphi_2 = 94, 91, 108, -75^\circ$ respectively), the ring N(6)–C(30) shows a conformation intermediate between 'twist' and 'envelope' ($q_2 = 0.12$ Å, $\varphi_2 = 54^\circ$), and N(4)–C(20) shows only a little puckering ($q_2 = 0.04$ Å, $\varphi_2 = -130^\circ$). The dimers are packed only by a few van der Waals contacts some of which involve one disordered ethanol molecule.

The structure of (2) consists of dimeric molecules (Figure 3) in

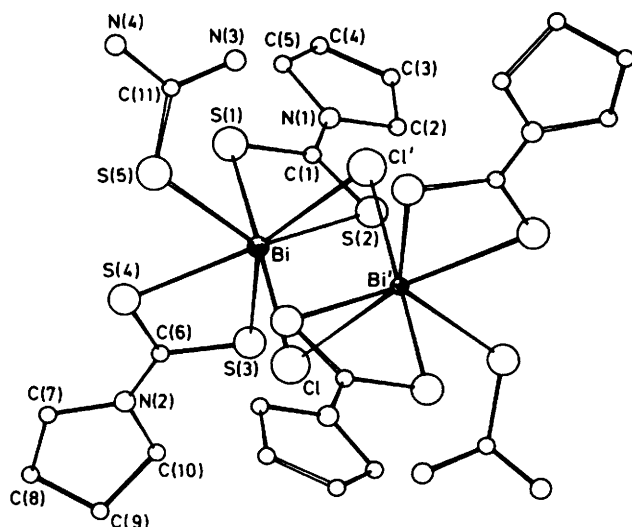


Figure 3. Projection of the complex (2)

which the bismuth atoms are connected by two centrosymmetric chlorines with asymmetric bridges [Table 4(b)] in a similar way to that in other Bi complexes.^{1,2,15} The four atoms involved in the bridges as a result of symmetry requirements are planar, the Bi...Bi separation is 4.603(2) Å, and the angle subtended at the chlorine is 97.9(1)°. The bond distances and angles in the *pcdt* molecules resemble those found in (1): the C-S bonds show no significant differences [Table 4(b)] and the C-C and C-N bond lengths are in the range expected. The conformations of the two rings are different: N(2)-C(10) has a 'twist' conformation ($q_2 = 0.33$ Å, $\varphi_2 = -82^\circ$) whereas N(1)-C(5) show a conformation intermediate between 'twist' and 'envelope' ($q_2 = 0.10$ Å, $\varphi_2 = 54^\circ$). The two S₂CN groups are planar and their mean planes form a dihedral angle of 91.7(2)°; bismuth lies 0.211(4) and 0.219(3) Å respectively from the S(1), S(2), C(1), N(1) and S(3), S(4), C(6), N(2) planes. The planar thiourea molecule [the displacement of Bi from this plane is 1.203(4) Å]

is involved in the following three hydrogen-bond interactions: N(3)-H(17) 0.98 Å, H(17)...Clⁱ 2.297 Å, N(3)...Clⁱ 3.234(4) Å, N(3)-H(17)...Clⁱ 160°; N(3)-H(18) 0.96 Å, H(18)...Clⁱⁱ 2.434 Å, N(3)...Clⁱⁱ 3.290(10) Å, N(3)-H(18)...Clⁱⁱ 148°; N(4)-H(19) 0.98 Å, H(19)...S(5ⁱⁱⁱ) 2.454 Å, N(4)...S(5ⁱⁱⁱ) 3.420(10) Å, N(4)-H(19)...Clⁱⁱⁱ 170° ($i = \bar{x}, \bar{y}, \bar{z}$; $ii = x, y, 1 + z$; $iii = 1 - x, \bar{y}, 1 - z$), which together with the other non-bonding contacts are responsible for the packing in the crystal.

References

- L. P. Battaglia and A. Bonamartini Corradi, *J. Chem. Soc., Dalton Trans.*, 1983, 2425.
- L. P. Battaglia and A. Bonamartini Corradi, *J. Chem. Soc., Dalton Trans.*, 1981, 23.
- L. P. Battaglia, A. Bonamartini Corradi, M. Nardelli, and M. E. Vidoni Tani, *J. Chem. Soc., Dalton Trans.*, 1978, 583.
- L. P. Battaglia, A. Bonamartini Corradi, G. Pelizzi, and M. E. Vidoni Tani, *J. Chem. Soc., Dalton Trans.*, 1977, 1141.
- A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
- 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1968, vol. 3, p. 210.
- G. Sheldrick, SHELX System of Computing Programs, University of Cambridge, 1976.
- C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1976, 791.
- C. L. Raston, G. L. Rowbottom, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 1372 and refs. therein.
- J. Albertsson, Å. Oskarsson, K. Oskarsson, K. Stahl, C. Svensson, and I. Ymén, *Acta Crystallogr., Sect. B*, 1980, **36**, 3072.
- C. A. Kavounis, S. C. Kokkou, P. J. Rentzeperis, and P. Karagiannidis, *Acta Crystallogr., Sect. B*, 1980, **36**, 2954.
- P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1972, 1163.
- P. W. G. Newman, C. L. Raston, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1973, 1332.
- D. Cremer and J. A. Pople, *J. Am. Chem. Soc.*, 1975, **97**, 1354.
- B. Aurivillius and C. Stålhandske, *Acta Chem. Scand., Ser. A*, 1978, **32**, 715.

Received 9th May 1985; Paper 5/770