The Lewis Acidity of Organylbismuth(III) Compounds. New Organylbismuth(III) Dithiocarbamate Chemistry. The Crystal and Molecular Structure of Bis(diethyldithiocarbamato)phenylbismuth(III) and Bis(diethyldithiocarbamato)-[2-(2′-pyridyl)phenyl]bismuth(III)*

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The compound $BiBr_2L$ [L = 2-(2′-pyridyl)phenyl] has been prepared *via* a *trans*metallation reaction between $BiBr_3$ and [HgCl(L)]. It reacts with $[NEt_4]I$ and $Na(O_2CEt)$ to give the ionic derivatives $[NEt_4][BiBr_2I(L)]$ and $Na[BiBr_2(O_2CEt)L]$. I.r. evidence suggests that the co-ordination of the extra ligands is accompanied by a reduction of the strength of the Bi–N interaction. The compound undergoes a substitution reaction with $Na(S_2CNEt_2)$ to give $[Bi(S_2CNEt_2)_2L]$ (**1**), and a new preparation of $[BiPh(S_2CNEt_2)_2]$, (**2**), *via* $[BiPh(O_2CCH{=}CHCO_2H)_2]$ is reported. Some ^{13}C n.m.r. data are presented and, in particular, the first definitive assignments of *ipso*-carbon resonances in arylbismuth compounds are given. The crystal and molecular structures of compounds (**1**) and (**2**) determined from three dimensional *X*-ray data are compared. Compound (**1**) is triclinic, space group $P\bar{1}$ with $a = 10.126(1)$, $b = 10.447(2)$, $c = 12.512(8)$ Å, $\alpha = 82.06(4)$, $\beta = 71.27(4)$, $\gamma = 86.92(1)°$, and $Z = 2$; $R = 0.0297$ for 4 063 observed reflections. The co-ordination about bismuth is pseudo-pentagonal bipyramidal with four diethyldithiocarbamato S atoms and the pyridyl N atom constituting the equatorial plane, and the phenyl carbon atom and the lone pair of electrons occupying the apical positions. The compound is essentially monomeric with two long contacts [Bi ••• Bi′ 3.954(1) and Bi ••• S′ 3.876(2) Å] to a neighbouring molecule. Bond lengths are Bi–C 2.263(7), Bi–S 2.766(2)—2.895(2), and Bi–N 2.553(6) Å. Compound (**2**) is monoclinic, space group $P2_1/c$, with $a = 14.796(7)$, $b = 9.437(9)$, $c = 16.942(8)$ Å, $\beta = 109.50(5)$, and $Z = 4$; $R = 0.0374$ for 3 017 observed reflections. The co-ordination about bismuth is also pseudo-pentagonal bipyramidal with the equatorial plane comprising the four diethyldithiocarbamato sulphur atoms and a bridging interaction with a sulphur in a centrosymmetrically related molecule, the phenyl carbon atom and the lone pair of electrons are located in the apical positions. Bond lengths are Bi–C 2.241(10), Bi–S 2.671(2)—2.942(2), and Bi ••• S′ 3.421(2) Å.

The study of organylbismuth compounds is a relatively neglected area of Main Group chemistry. The topic has however been well served by the review literature.[1a,b] Freedman and Doak[2] updated their survey and a further useful account is included in ref. 3. Despite the fact that bismuth is a relatively rare element (crystal abundance 0.008 p.p.m.), the market currently seeks further outlets for the element and its compounds, thus it is timely to expand this area of chemistry.

In this paper, our first contribution to the field, we present new results on some organylbismuth(III) dithiocarbamates. Our objective was to gain information on the Lewis acidity of $BiRX_2$ species where R = an organic group, and X = an anionic function; thus $[Bi^{III}R(S_2CNEt_2)_2]$ is an example. The compound $[BiMe(S_2CNEt_2)_2]$ is well known[4,5] and its structure has been determined. Bismuth achieves a pentagonal bipyramidal geometry *via* S-bridging within dimers. The compound $[BiPh(S_2CNEt_2)_2]$ may be prepared from the reaction of sodium diethyldithiocarbamate with either $BiPh_2Cl$[6] (*via* a redistribution reaction, the other product being $BiPh_3$), or with $BiPhBr_2$.[7] Its structure is reported in this paper. We were particularly interested to assess the preference of bismuth for S or N donors. Examples of bismuth nitrogen co-ordination are well known; all three nitrogen atoms in $[\mathrm{Bi(O_2CBu^t{=}CNC{=}CBu^tO)_3}]$ are co-ordinated to give a nine-co-ordinate complex.[8] Of more relevance to the present work, tris(dithiocarbamato) complexes containing antimony give only 'solvates' with 4,4′-bipyridyl whereas, by contrast, in $[Bi(S_2CNEt_2)X_2(py)_3]$ (X = Cl or I) the pyridines (py) are loosely co-ordinated to give a seven-co-ordinate complex.[9] When $[Bi(S_2CNEt_2)I_2]$ reacts with 2,2′-bipyridyl (bipy) or with 2,2′; 6′,2″-terpyidyl (terpy), dimeric $[(bipy)I(Et_2NCS_2)BiI_2Bi(S_2CNEt_2)I(bipy)]$ and monomeric $[BiI_2(S_2CNEt_2)(terpy)]$ are formed.[10] Hence it is already implicit within the literature that bismuth(III) centres have some affinity for –N=ligands; we wished to investigate if this were also true for organylbismuth(III) species.

The approach we have adopted is to 'anchor' the nitrogen donor to the organic group attached to bismuth and for this purpose we have selected *ortho*-bismuthated 2-phenylpyridine. Thus by synthesising and determining the crystal and molecular structures of $[BiPh(S_2CNEt_2)_2]$ and $[Bi(S_2CNEt_2)_2L]$ [L = 2-(2′-pyridyl)phenyl] we can make some assessment of the relative affinity of bismuth for –N= and S donors. In addition we take the opportunity to report on other preparative work related to the study of the Lewis acidity of $BiRX_2$, together with appropriate spectroscopic data for the new organylbismuth compounds.

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Experimental

Synthesis of Organylbismuth Compounds.—[2-(2′-Pyridyl)-phenyl]mercury(II) chloride was prepared by the literature method.[11]

[2-(2′-*Pyridyl*)*phenyl*]*bismuth*(III) *dibromide*. [2-(2′-Pyridyl)phenyl]mercury(II) chloride (4.0 g, 10 mmol) in dry dioxane (40 cm^3) was added to a solution of bismuth tribromide (4.49 g, 10 mmol) in dry dioxane (20 cm^3). The mixture was refluxed under dinitrogen for 4 h resulting in the formation of a pale yellow compound. The solution was filtered hot, and the precipitate was washed with absolute ethanol and recrystallised from acetonitrile. Yield 76%, m.p. 248—250 °C (Found: C, 26.0; H, 1.60; N, 2.70. $C_{11}H_8BiBr_2N$ requires C, 25.2; H, 1.55; N, 2.70%).

Bis(*diethyldithiocarbamato*)[2-(2′-*pyridyl*)*phenyl*]*bismuth*(III). [2-(2′-Pyridyl)phenyl]bismuth(III) dibromide (0.53 g, 1.0 mmol) in dry acetonitrile (20 cm^3) was mixed with a solution of sodium diethyldithiocarbamate (0.38 g, 2.0 mmol) in dry acetonitrile (15 cm^3). The mixture was refluxed under dinitrogen for 3 h, filtered hot and set aside to cool. Pale yellow crystals were formed in 88% yield, m.p. 222—224 °C (Found: C, 37.8; H, 4.10; N, 6.15. $C_{21}H_{28}BiN_3S_4$ requires C, 38.2; H, 4.25; N, 6.4%).

Reaction of [2-(2′-*Pyridyl*)*phenyl*]*bismuth*(III) *Dibromide*.—*With sodium propionate*. The above method was followed with the substitution of sodium propionate in dry acetonitrile. An 84% yield of a product with m.p. > 250 °C was obtained [Found: C, 28.1; H, 2.35; N, 2.15; Na, 4.1 (by atomic absorption) $C_{14}H_{13}BiBr_2NNaO_2$ {Na[$BiBr_2(O_2CEt)L$]} requires C, 27.1; 2.10; N, 2.30; Na, 3.70%].

With Tetraethylammonium iodide. The above procedure was repeated using tetraethylammonium iodide. A product, which was recrystallised from nitromethane, with m.p. 155—157 °C was obtained in 85% yield (Found: C, 28.6; H, 3.90; N, 3.75. $C_{19}H_{28}BiBr_2IN_2$, {[NEt_4][$BiBr_2I(L)$]} requires C, 29.2; H, 3.60; N, 3.60%).

Phenylbismuth(III) *Dimaleate*.—A solution of maleic acid (1.32 g, 11.5 mmol) in dry diethyl ether (30 cm^3) was added to a solution of triphenylbismuthine (2.5 g, 5.7 mmol) in dry diethyl ether (30 cm^3) and refluxed under dry nitrogen for 3 h. The solution was quickly filtered prior to cooling and the separated solid was dried *in vacuo*, yield 26%, m.p. >300 °C. Slow evaporation of the filtrate afforded a second as yet uncharacterised product (Found: C, 32.2; H, 1.50. $C_{14}H_{11}BiO_8$ requires C, 32.5; H, 2.10%).

Bis(*diethyldithiocarbamato*)*phenylbismuth*(III).—This material was obtained from the following reaction: sodium diethyldithiocarbamate (0.44 g, 2.0 mmol) in dimethyl suphoxide– nitromethane–water (1:1:1) solution was added to a solution of phenylbismuth(III) dimaleate (1.0 g, 2.0 mmol), also in the above solvent mixture, to give a total volume of 100 cm^3. A small quantity of [NEt_4]ClO_4 was added and the mixture was refluxed under dinitrogen for 5 h, then filtered hot. The filtrate was set aside to evaporate slowly to give a mixture of white and yellow crystals. The white crystals were separated and shown to be $BiPh_3$ (m.p. 77—78 °C, lit.,[2] 77.6 °C). The yellow crystals were recrystallised from ethanol. Crystals suitable for *X*-ray crystallography were grown by low temperature recrystallisation from ethanol over 4 weeks.

Physical Measurements.—Melting points (uncorrected) were determined with a Galenkamp electrically heated apparatus. Conductivity measurements (10^{-3} mol dm^{-3} solutions) were made at room temperature with a Mullard bridge and dip cell with bright platinum electrodes (type E7591/B). I.r. spectra were recorded for KBr discs with a Perkin-Elmer 1710 FTIR instrument, n.m.r. spectra (^1H, ^{13}C, and ^{14}N) with a Bruker AC300 spectrometer (internal standard $SiMe_4$, external standard $NaNO_3$ in aqueous solution). Table 1 lists relevant i.r. data and Table 2 the n.m.r. data.

Structural Investigations.—The crystal and molecular structures of bis(diethyldithiocarbamato)[2-(2′-pyridyl)phenyl]bismuth(III), compound (**1**), and of bis(diethyldithiocarbamato)-phenylbismuth(III), compound (**2**), were determined.

After preliminary study of suitable crystals by photographic methods, final cell dimensions and reflection intensities were measured with graphite-monochromated Mo-K_α radiation on an Enraf-Nonius CAD-4 diffractometer, operating in the ω—2θ scan mode. Three standard reflections were monitored at regular intervals. Empirical absorption corrections[12] [range of transmission factors (**1**), 1.039—1.895; (**2**), 1.012—1.756] were applied. Details of crystal and experimental parameters are given in Table 3.

Both structures were solved by Patterson and Fourier methods. As it was not possible to distinguish all the hydrogen positions in either structure, hydrogen atoms were placed in calculated positions (C–H 1.08 Å) and allowed to 'ride' on their respective carbon atoms in the subsequent least-squares refinements. Anisotropic thermal parameters were used for all the non-hydrogen atoms. Atomic co-ordinates for complexes (**1**) and (**2**) are given in Tables 4 and 5, bond lengths and bond angles in Tables 6 and 7.

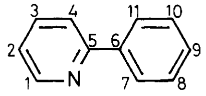
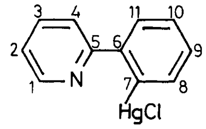
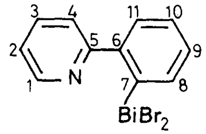
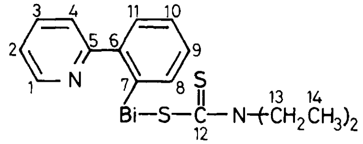
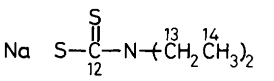
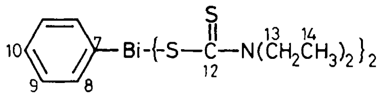
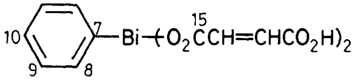
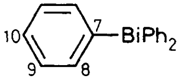
Computations were carried out on the Birmingham University Honeywell computer with SHELXS 86[13] and SHELX 76.[14] Structures were drawn using PLUTO[15] at the University of Manchester Regional Computer Centre.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Table 1. I.r. data (cm^{-1}) for the new organobismuth complexes; L = 2-(2′-pyridyl)phenyl

Compound	Ring deformations				
	In plane	Out of plane	$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	$\Delta\nu(CO_2)$
2-phenylpyridine	604	405			
[HgCl(L)]	625	420			
[NEt_4][$BiBr_2(L)$]	629	416, 406			
Na[$BiBr_2I(L)$]	636	409			
Na[$BiBr_2(O_2CEt)L$]	637	407	1 617	1 431	166
Na(O_2CEt)			1 561	1 430	131
[$Bi(S_2CNEt_2)_2L$]	631	420			
[$BiPh(O_2CCH{=}CHCO_2H)_2$]			1 533	1 261	272
$K_2[O_2CCH{=}CHCO_2]$		1 436	1 297	139	157

Table 2. ^{13}C N.m.r. data for organylbismuth compounds. Solvents are indicated and all chemical shifts are p.p.m. *vs.* $SiMe_4$ as internal standard

Compound	Solvent	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}	C^{13}	C^{14}
	$CDCl_3$	149.1	119.1	136.2	121.5	156.7	138.8	126.3		128.1		126.3			
	$CDCl_3$	149.1	120.9	138.3	123.4	155.9	141.3	147.9	137.8	128.2	129.2	127.1			
	$(CD_3)_2SO$	148.3	121.9	139.2	124.3	162.9	147.4	140.9	134.6	128.6	130.4				
	$(CD_3)_2SO$	147.2	121.2	139.6	123.7	160.6	146.7	141.5	133.2	128.2		127.6	201.2	47.7	12.0
 $\mathrm{Na\ S{-}\overset{S}{\overset{\|}{C}}{-}N(CH_2CH_3)_2}$	D_2O												208.2	51.3	14.0
	$CDCl_3$								138.6	131.3	127.2		198.9	47.5	11.5
	$(CD_3)_2SO$							133.8	132.3	131.3	130.2		168.0 (C=O)		
	$CDCl_3$							155.0	137.5	130.5	127.7				

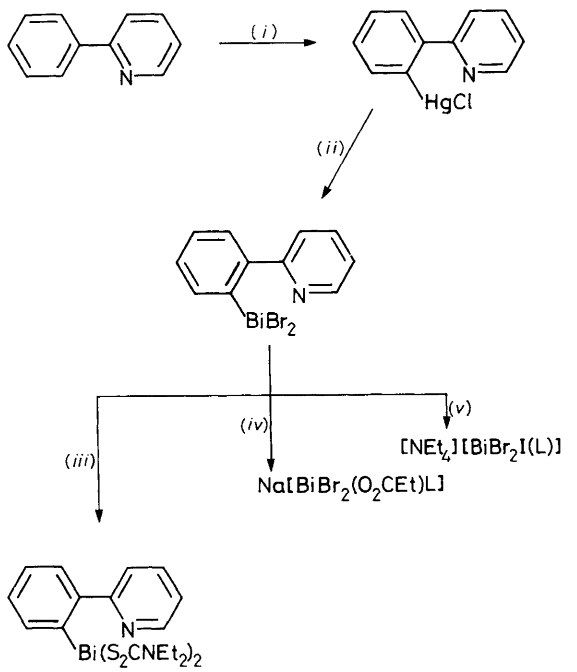
Discussion

(*a*) *Synthetic Studies.*—We wished to obtain information on the Lewis acidity of organylbismuth species of the type $BiRX_2$ and, to this end, decided to 'anchor' the donor group to the organic moiety R and to study the reactions of the resulting new organylbismuth compounds with additional ligands such as carboxylate, dithiocarbamate, and iodide (see Scheme). We recently pioneered the use of [2-(2-pyridyl)phenyl]mercury(II) chloride to prepare some interesting organyltellurium compounds,[16] and others[17] have now used the reagent as a convenient route to transition-metal complexes which can be viewed as analogues of C,N bonded bipyridine compounds. It was therefore decided to treat the mercury derivative of 2-phenylpyridine with $BiBr_3$, selected for its slower rate of hydrolysis over $BiCl_3$. The reaction proceeded smoothly to afford $[BiBr_2(L)]$, [L = 2-(2′-pyridyl)phenyl].

[2-(2′-Pyridyl)phenyl]bismuth(III) bromide is stable and isolable, in contrast to phenylbismuth dibromide which, although known in solution,[18] has not to our knowledge been isolated as a solid; it may be isolated by complex formation,[19] *e.g.* $[BiPhBr_2(bipy)]$. There is then the implication that a bismuth–nitrogen co-ordinate bond has been formed. Many years ago it was established that the base tri-(2-pyridyl)amine (tripyam) may function as a bidentate or tripodal terdentate ligand to copper(II)[20] and in that study it was noted that the 2-pyridyl out-of-plane ring deformation mode, φ(CC), close to 405 cm^{-1} in the i.r. region was very sensitive to the co-ordination of the 2-pyridyl group. By analogy with this work, i.r. data for $BiRBr_2$ (Table 1) suggest that the Bi–N interaction must at best be weak. The mercury derivative, [HgCl(L)], is included for comparison and a recent structure determination[21] does indeed confirm that the Hg–N interaction is weak. An interesting feature of the spectrum of $[BiBr_2(L)]$ is that there is the implication that two environments exist for the 2-pyridylphenyl group in this compound, one weakly co-ordinated and the other unco-ordinated; it is virtually certain that the compound cannot be monomeric in the solid state, however there is not evidence

Table 3. Crystal and experimental parameters

Compound	(1)	(2)
Molecular formula	$C_{21}H_{28}BiN_3S_4$	$C_{16}H_{25}BiN_2S_4$
M	659.7	582.6
Crystal size (mm)	1.00 × 0.35 × 0.25	0.32 × 0.25 × 0.03
a/Å	10.126(1)	14.796(7)
b/Å	10.447(2)	9.437(9)
c/Å	12.512(8)	16.942(8)
α/°	82.06(4)	90
β/°	71.27(4)	109.50(5)
γ/°	86.92(1)	90
U/A^3	1 241.4	2 229.9
Space group	$P\bar{1}$	$P2_1/c$
Z	2	4
D_c/g cm^{-3}	1 765	1 735
F(000)	644	1 128
μ(Mo-K_α)/mm^{-1}	7.412	8.240
Data collection range, θ/°(λ = 0.710 69 Å)	2—25	2—25
Unique data measured	4 346	3 916
Significant data $[I > 2.5\theta(I)]$	4 063	3 017
Least squares weight *g* $\{w[\sigma^2(F) + gF^2]^{-1}\}$	0.001	0.0001
Maximum shift/error in final least-squares cycle	0.06	0.48
R	0.0297	0.0374
R′	0.0545	0.0496
Residual electron density/e A^{-3}	−1.2 to 1.8	−1.1 to 1.4



Scheme. L = 2-(2′-pyridyl)phenyl; (*i*) $Hg(O_2CMe)$–LiCl; (*ii*) $BiBr_3$; (*iii*) $Na(S_2CNEt_2)$; (*iv*) $Na(O_2CEt)$; (*v*) $[NEt_4]I$

Table 4. Fractional atomic co-ordinates (× 10^4, × 10^5 for Bi) with estimated standard deviations (e.s.d.s) in parentheses for compound (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Bi	41 062(2)	49 682(2)	16 594(2)	C(8)	6 356(9)	6 518(9)	3 947(7)
S(1)	2 027(2)	3 092(2)	2 346(2)	C(9)	7 779(9)	6 475(10)	3 413(10)
S(2)	4 549(2)	2 659(2)	3 078(2)	C(10)	8 287(8)	6 053(9)	2 348(9)
S(3)	2 123(2)	6 065(2)	714(2)	C(11)	7 359(8)	5 677(8)	1 886(8)
S(4)	4 632(2)	7 546(2)	471(2)	C(12)	3 031(7)	2 101(7)	2 991(6)
N(1)	5 984(6)	5 707(6)	2 391(5)	C(13)	1 329(9)	353(9)	3 385(8)
N(2)	2 635(7)	884(6)	3 425(6)	C(14)	1 595(16)	− 330(13)	2 342(12)
N(3)	2 612(7)	8 452(6)	−360(6)	C(15)	3 422(10)	−3(9)	3 973(9)
C(1)	3 074(7)	5 843(6)	3 287(6)	C(16)	2 994(12)	49(10)	5 241(9)
C(2)	1 654(7)	5 932(8)	3 714(7)	C(17)	3 078(7)	7 479(7)	212(6)
C(3)	1 033(8)	6 396(7)	4 764(7)	C(18)	3 531(11)	9 577(12)	−871(10)
C(4)	1 843(8)	6 718(8)	5 371(7)	C(19)	2 856(17)	10 757(12)	−1 323(17)
C(5)	3 270(8)	6 657(7)	4 938(7)	C(20)	1 281(10)	8 367(10)	571(9)
C(6)	3 909(7)	6 209(6)	3 882(6)	C(21)	1 420(13)	7 836(13)	−1 650(11)
C(7)	5 458(7)	6 144(6)	3 411(6)				

Table 5. Fractional atomic co-ordinates (× 10^4, × 10^5 for Bi) with e.s.d.s in parentheses for compound (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Bi	19 059(2)	4 297(4)	5 661(2)	C(6)	873(6)	1 250(10)	−1 401(5)
S(1)	2 937(2)	−154(3)	2 335(2)	C(7)	1 142(8)	2 383(12)	−2 597(7)
S(2)	3 747(2)	1 206(4)	1 138(2)	C(8)	1 563(12)	1 353(16)	−3 040(10)
S(3)	2 082(2)	1 501(3)	838(2)	C(9)	−493(7)	1 510(11)	−2 702(6)
S(4)	171(2)	413(3)	−928(1)	C(10)	−1 088(7)	2 750(13)	−2 612(8)
N(1)	4 644(5)	1 084(10)	2 769(5)	C(11)	2 209(7)	−1 772(11)	227(6)
N(2)	528(5)	1 677(8)	−2 183(5)	C(12)	1 629(11)	−2 849(14)	296(8)
C(1)	3 841(6)	723(11)	2 137(6)	C(13)	1 781(15)	−4 199(15)	63(10)
C(2)	5 443(7)	1 849(13)	2 622(8)	C(14)	2 479(15)	−4 418(18)	−292(11)
C(3)	4 777(7)	736(14)	3 642(7)	C(15)	3 016(12)	−3 365(23)	−404(9)
C(4)	4 450(9)	1 897(19)	4 088(9)	C(16)	2 885(8)	−2 021(15)	−147(7)
C(5)	6 165(9)	882(19)	2 492(11)				

Table 6. Bond lengths (Å) and angles (°) with e.s.d.s in parentheses for compound (**1**)

Bi–S(1)	2.798(2)	S(4)–C(17)	1.713(7)	N(3)–C(20)	1.463(11)	C(8)–C(9)	1.381(13)
Bi–S(2)	2.895(2)	N(1)–C(7)	1.350(9)	C(1)–C(2)	1.367(10)	C(9)–C(10)	1.390(15)
Bi–S(3)	2.766(2)	N(1)–C(11)	1.332(9)	C(1)–C(6)	1.390(10)	C(10)–C(11)	1.351(13)
Bi–S(4)	2.878(2)	N(2)–C(12)	1.340(10)	C(2)–C(3)	1.402(11)	C(13)–C(14)	1.515(15)
Bi–N(1)	2.553(6)	N(2)–C(13)	1.479(10)	C(3)–C(4)	1.365(12)	C(15)–C(16)	1.512(15)
Bi–C(1)	2.263(7)	N(2)–C(15)	1.436(10)	C(4)–C(5)	1.372(11)	C(18)–C(19)	1.507(14)
S(1)–C(12)	1.714(7)	N(3)–C(17)	1.316(10)	C(5)–C(6)	1.404(10)	C(20)–C(21)	1.493(16)
S(2)–C(12)	1.714(7)	N(3)–C(18)	1.478(11)	C(6)–C(7)	1.489(10)		
S(3)–C(17)	1.737(7)			C(7)–C(8)	1.389(10)		
S(1)–Bi–S(2)	62.9(1)	N(1)–Bi–C(1)	70.8(2)	Bi–C(1)–C(2)	120.6(5)	C(8)–C(9)–C(10)	119.2(8)
S(1)–Bi–S(3)	76.9(1)	Bi–S(1)–C(12)	89.9(2)	Bi–C(1)–C(6)	118.6(5)	C(9)–C(10)–C(11)	118.2(7)
S(2)–Bi–S(3)	139.8(1)	Bi–S(2)–C(12)	86.7(3)	C(2)–C(1)–C(6)	120.6(7)	N(1)–C(11)–C(10)	123.3(8)
S(1)–Bi–S(4)	139.9(1)	Bi–S(3)–C(17)	91.1(2)	C(1)–C(2)–C(3)	119.6(7)	S(1)–C(12)–S(2)	120.2(4)
S(2)–Bi–S(4)	156.7(1)	Bi–S(4)–C(17)	87.9(3)	C(2)–C(3)–C(4)	120.1(7)	S(1)–C(12)–N(2)	120.2(5)
S(3)–Bi–S(4)	63.1(1)	Bi–N(1)–C(7)	113.1(4)	C(3)–C(4)–C(5)	120.6(7)	S(2)–C(12)–N(2)	119.7(6)
S(1)–Bi–N(1)	137.5(1)	Bi–N(1)–C(11)	127.1(5)	C(4)–C(5)–C(6)	119.9(7)	N(2)–C(13)–C(14)	111.0(8)
S(2)–Bi–N(1)	78.4(1)	C(7)–N(1)–C(11)	119.8(7)	C(1)–C(6)–C(5)	119.0(6)	N(2)–C(15)–C(16)	112.4(8)
S(3)–Bi–N(1)	138.3(1)	C(12)–N(2)–C(13)	122.1(7)	C(1)–C(6)–C(7)	121.0(6)	S(3)–C(17)–S(4)	117.9(4)
S(4)–Bi–N(1)	78.6(1)	C(12)–N(2)–C(15)	123.3(7)	C(5)–C(6)–C(7)	120.0(6)	S(3)–C(17)–N(3)	120.2(5)
S(1)–Bi–C(1)	89.5(2)	C(13)–N(2)–C(15)	114.6(7)	N(1)–C(7)–C(6)	116.1(6)	S(4)–C(17)–N(3)	121.9(6)
S(2)–Bi–C(1)	87.0(2)	C(17)–N(3)–C(18)	117.9(7)	N(1)–C(7)–C(8)	119.8(7)	N(3)–C(18)–C(19)	115.6(9)
S(3)–Bi–C(1)	91.6(2)	C(17)–N(3)–C(20)	120.8(7)	C(6)–C(7)–C(8)	124.2(7)	N(3)–C(20)–C(21)	113.3(9)
S(4)–Bi–C(1)	88.5(2)	C(18)–N(3)–C(20)	121.1(7)	C(7)–C(8)–C(9)	119.6(8)		

from the ^{13}C n.m.r. spectrum (Table 2) for inequivalent organic groups in dimethyl sulphoxide (dmso) solution.

The Lewis acidity of $[BiBr_2(L)]$ has been investigated by study of the reactions of the compound with (*a*) $[NEt_4]I$, (*b*) $Na(O_2CEt)$, and (*c*) $Na(S_2CNEt_2)$. For (*a*) and (*b*) acid–base reactions are observed. The salt $[NEt_4][BiBr_2I(L)]$ gave well formed crystals [unit cell: a = 12.077(16), b = 17.910(28), c = 13.419(26) Å; α = 90.00(14), β = 116.57(12), γ = 90.00(12)°] but unfortunately insufficient reflections were observed to resolve the structure. The compound was soluble in dmso, hence ^{14}N n.m.r. spectroscopy was used to confirm the presence of the cation. Two resonances were observed, a broad band at −45.4 p.p.m. and a very sharp band at −310.2 p.p.m. (both relative to aqueous $NaNO_3$ as external reference). Nitrogen-14 is a quadrupolar nucleus (I = 1), hence the sharp resonance is clearly from a species in which the micro-symmetry of the nitrogen atom is high, *i.e.* NEt_4^+.[22] It follows that the broad resonance arises from the low-symmetry pyridyl nitrogen atom and, indeed, 2-phenylpyridine in dmso gives a broad resonance at −56.0 p.p.m. Solubility problems prevented a comprehensive investigation of the ^{14}N n.m.r. spectra of the compounds reported in this paper (also the strongly co-ordinating dmso was a solvent of necessity rather than choice), hence we do not speculate as to the significance, if any, of the apparent deshielding of the pyridyl-nitrogen atom in the

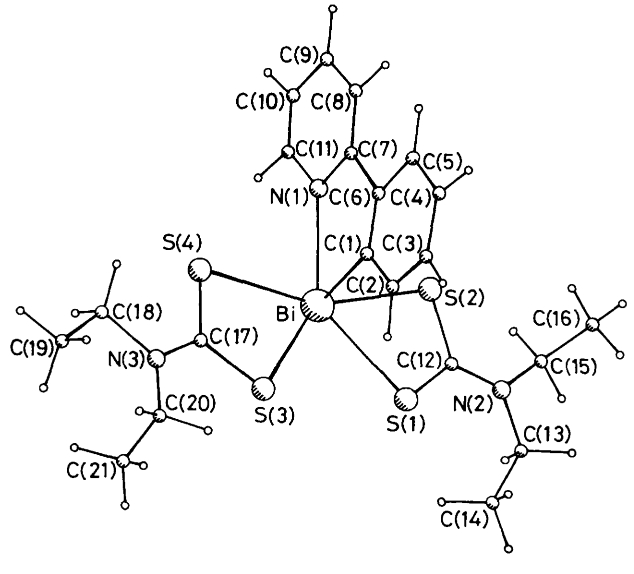


Figure 1. Molecular structure of bis(diethyldithiocarbamato)[2-(2′-pyridyl)phenyl]bismuth(III)

Table 7. Bond lengths (Å) and angles (°) with e.s.d.s in parentheses for compound (**2**)

Bi–S(1)	2.926(2)	N(2)–C(7)	1.479(12)
Bi–S(2)	2.671(2)	N(2)–C(9)	1.480(12)
Bi–S(3)	2.676(3)	C(2)–C(5)	1.477(17)
Bi–S(4)	2.942(2)	C(3)–C(4)	1.500(18)
Bi–C(11)	2.241(10)	C(7)–C(8)	1.486(17)
S(1)–C(1)	1.698(10)	C(9)–C(10)	1.502(15)
S(2)–C(1)	1.714(10)	C(11)–C(12)	1.360(16)
S(3)–C(6)	1.740(8)	C(11)–C(16)	1.371(15)
S(4)–C(6)	1.703(9)	C(12)–C(13)	1.374(19)
N(1)–C(1)	1.351(11)	C(13)–C(14)	1.372(25)
N(1)–C(2)	1.476(13)	C(14)–C(15)	1.325(24)
N(1)–C(3)	1.463(14)	C(15)–C(16)	1.376(21)
N(2)–C(6)	1.315(11)		
S(1)–Bi–S(2)	63.9(1)	C(7)–N(2)–C(9)	115.7(8)
S(1)–Bi–S(3)	144.0(1)	S(1)–C(1)–S(2)	121.0(5)
S(2)–Bi–S(3)	80.1(1)	S(1)–C(1)–N(1)	120.6(8)
S(1)–Bi–S(4)	152.5(1)	S(2)–C(1)–N(1)	118.4(7)
S(2)–Bi–S(4)	143.6(1)	N(1)–C(2)–C(5)	112.5(10)
S(3)–Bi–S(4)	63.5(1)	N(1)–C(3)–C(4)	112.9(11)
S(1)–Bi–C(11)	90.4(3)	S(3)–C(6)–S(4)	118.8(5)
S(2)–Bi–C(11)	94.6(3)	S(3)–C(6)–N(2)	119.6(7)
S(3)–Bi–C(11)	92.0(3)	S(4)–C(6)–N(2)	121.6(6)
S(4)–Bi–C(11)	88.1(2)	N(2)–C(7)–C(8)	111.9(9)
Bi–S(1)–C(1)	83.2(3)	N(2)–C(9)–C(10)	111.9(8)
Bi–S(2)–C(1)	91.2(3)	Bi–C(11)–C(12)	119.0(8)
Bi–S(3)–C(6)	92.8(3)	Bi–C(11)–C(16)	121.1(9)
Bi–S(4)–C(6)	84.8(3)	C(12)–C(11)–C(16)	119.3(11)
C(1)–N(1)–C(2)	122.2(9)	C(11)–C(12)–C(13)	120.0(15)
C(1)–N(1)–C(3)	122.0(8)	C(12)–C(13)–C(14)	119.0(17)
C(2)–N(1)–C(3)	115.8(8)	C(13)–C(14)–C(15)	121.6(15)
C(6)–N(2)–C(7)	121.5(8)	C(14)–C(15)–C(16)	119.5(16)
C(6)–N(2)–C(9)	122.8(8)	C(11)–C(16)–C(15)	120.4(16)

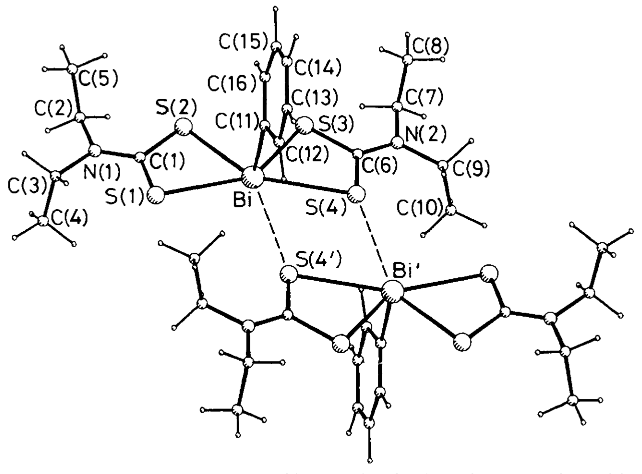


Figure 2. Molecular structure of bis(diethyldithiocarbamato)phenylbismuth(III) dimer

presence of bismuth. It is noted from Table 1 that the φ(CC) vibration at 409 cm^{-1} implies at best an extremely weak Bi–N interaction in the solid.

The reaction of sodium propionate with [BiBr$_2$(L)] affords Na[BiBr$_2$(O$_2$CEt)L], a high-melting somewhat intractable solid. The i.r. data (Table 1) certainly suggest the propionate group to be co-ordinated. The separation, Δν, of the ν_{asym}(CO$_2$) and ν_{sym}(CO$_2$) bands is a good indication of the mode of co-ordination of a carboxylate group;[23] the value of Δν for this compound is 166 cm^{-1} which implies that the carboxylate is symmetrically bidentate or symmetrically bridging, given that the value is close to that for Na(O$_2$CEt), *i.e.* 131 cm^{-1}. If the group were unsymmetrically bidentate or monodentate the separation would be much greater, for example the monodentate acetato complex tricyclohexyltin(IV) acetate[24] gives Δν = 361 cm^{-1} and SnMe$_2$(O$_2$CMe)$_2$,[25] with unsymmetrically bidentate acetato groups, shows Δν = 227 cm^{-1}. Also the i.r. data suggest the 2-pyridyl group to be either non- or very weakly co-ordinated.

The reaction of [BiBr$_2$(L)] with I$^-$ or EtCO$_2$$^-$ results in the addition of the anionic group and, according to the i.r. data, a significant weakening of the Bi–N bond. By contrast, reaction with Na(S$_2$CNEt$_2$) gives a substitution reaction to afford [Bi(S$_2$CNEt$_2$)$_2$L] in which the 2-pyridyl group interacts with bismuth at least as strongly as it interacts with mercury in [HgCl(L)] (Table 1); this interaction is confirmed crystallographically (see below). Recently we had hoped to compare the competitive affinity of tellurium(IV) for S and N donors and we synthesised (2-phenylazophenyl-*C*,*N'*)tellurium(IV) tris(diethyldiethiocarbamate)[26] with a view to comparing the structure to that of TePh(S$_2$CNEt$_2$)$_3$;[27] however it transpired that the first compound was a charge transfer complex of the tellurium(II) compound and dithiuram disulphide. Since Bi^{III} is pseudo-isoelectronic with Te^{IV} and should be less likely to give reductive elimination of the disulphide, we decided to compare the structures of [Bi(S$_2$CNEt$_2$)$_2$L] and [BiPh(S$_2$CNEt$_2$)$_2$]. The latter compound was prepared *via* phenylbismuth dimaleate, the preparation of which is reported here. The 'substitution' reaction is not straightforward since *two* products were noted; the yellow crystals of [BiPh(S$_2$CNEt$_2$)$_2$] and white crystals which proved to be BiPh$_3$. The identity of triphenylbismuth was positively confirmed by solving the crystal structure; the parameters determined were in good agreement with an earlier determination[28] and it is unnecessary to present details. It is probable that a disproportionation reaction of the dimaleate occurs simultaneously with the substitution reaction.

(*b*) ^{13}C *N.M.R. Data*.—The assignments of Table 2 follow closely those developed for tellurated 2-phenylpyridines[11] and detailed discussion is not warranted. One point is however worth exploring more deeply; we were surprised to note that Freedman and Doak[1b] reported that the resonance of the *ipso* carbon atoms of BiPh$_3$ was at −0.12 p.p.m. *vs.* SiMe$_4$. It was difficult to believe that this carbon should be so strongly shielded compared to similar atoms in organyl-tellurium[11] and -mercury compounds.[29] Consultation of the original paper[30] revealed that the authors made no assignment of the *ipso* resonance and that the quoted figure of −0.12 referred to the Taft constant. We have now been able to provide an unambiguous assignment of the *ipso* carbon resonance of BiPh$_3$ both by using longer delay times between pulses and also using the QUAT-D pulse sequence. The value is 155 p.p.m. *vs.* SiMe$_4$. *ipso*-Carbon resonances are also assigned for some other compounds reported here (Table 2); the resonances are usually broad, a consequence of the nuclear spin (9/2) of the 100% abundant ^{209}Bi.

(*c*) *Structural Investigation of Bis*(*diethyldithiocarbamato*)[2-(2'-*pyridyl*)*phenyl*]*bismuth*(III), (**1**).—The structure is shown in Figure 1. The co-ordination about bismuth can be considered pseudo-pentagonal bipyramidal, with four sulphur atoms from the dithiocarbamato groups and the pyridyl nitrogen atom making up the equatorial plane, and the phenyl carbon atom C(1) and the bismuth lone pair of electrons defining the axis. The deviation from ideal pentagonal bipyramidal values is due to the constraints imposed on the system by the bite of the 2-pyridylphenyl and dithiocarbamato ligands. Apart from the N(1)–Bi–C(1) angle of 70.8 (ideal 90) and S(2)–Bi–S(4), 156.7 (ideal 144°), all angles at bismuth are within 10° of theoretical values. The 'BiS_4' equatorial grouping is coplanar to within ± 0.06 Å with the nitrogen atom displaced by 0.067 Å. The distance Bi–C(1) [2.263(7) Å] is in good agreement with the sum of the Pauling covalent single-bond radii for sp^2-hybridised carbon and bismuth (2.26 Å) [31,32] and with the values found for triphenylbismuth [2.21—2.25(2) Å].[28] The Bi–N distance is of particular note. At 2.553(6) Å it is significantly longer than the sum of the covalent radii for a Bi–N single bond (2.22 Å),[31,32] but is well within the van der Waals distance. This observation lends support to the interpretation of the i.r. data presented earlier. The distance lies at the lower end of the range reported for the same interaction in other bismuth compounds [9,10] which lie in the range 2.56—2.86 Å. Similar short metal–nitrogen secondary interactions have been reported for a number of tellurium compounds incorporating the 2-(2′-pyridyl)phenyl group.[11,16] Then, as with this material, the metal–nitrogen interaction holds the 2-(2′-pyridyl)phenyl ligand in a virtually planar geometry. In the present structure the relative twist of the mean planes is only 4.0(1)° and the ligand is planar to within ± 0.06 Å, with the bismuth atom situated 0.18 Å from the plane.

Although all four bismuth–sulphur distances are longer than the theoretical value for a covalent Bi–S single bond (2.55 Å),[31,32] they are comparable with previously reported Bi–S values and may be categorised similarly. Each dithiocarbamato ligand can be considered to be linked to the central bismuth atom *via* one short bismuth–sulphur bond and one long bond.[33] The two short Bi–S bonds [2.798(2) and 2.766(2) Å] lie at the upper limit for this type of bond [2.595(5)—2.775(5) Å];[4,34] the two long Bi–S bonds [2.878(2) and 2.895(2) Å] fall at the lower end of their range [2.886(4)—2.965(4) Å].[4,34] The bond lengths and angles within each dithiocarbamato ligand fall within the range of standard values. The S_2CNC_2 portion of each dithiocarbamato group is essentially planar (± 0.04 Å), with a dihedral angle between the mean plane for each ligand and the mean plane of the bismuth 2-(2′-pyridyl)phenyl moiety of 88.5(1) and 92.7(1)°. The $Bi(S_2CNC_2)_2$ equatorial grouping is planar to within ± 0.13 Å with N(1) displaced by 0.68 Å. The closest intermolecular contacts involving the bismuth atom are with the molecule at $1 - x, 1 - y, -z$, Bi ··· Bi′ 3.954(1) and Bi ··· S(4′) 3.876(2) Å. The angles C(1)–Bi ··· Bi′ and C(1)–Bi ··· S(4′) are 155.6(2) and 160.9(2)°. Atoms Bi′ and S(4′) thus straddle the other apex of the pentagonal bipyramid. Any bonding interaction at this range must be considered extremely weak.

Bis(diethyldithiocarbamato)phenylbismuth(III), **(2)**.—The structure of compound **(2)** is shown in Figure 2. Although the bismuth atom is only five-co-ordinate, the co-ordination geometry is similar to that in compound **(1)**. The four sulphur atoms and the bismuth are coplanar to within ± 0.02 Å. The fifth contact completing the equatorial pentagonal co-ordination is to S(4′) of the centrosymmetrically related molecule at 3.421(2) Å, and 0.58 Å from the equatorial plane. The pertinent angles are S(1)–Bi ··· S(4′) 88.0(1) and S(4)–Bi ··· S(4′) 64.9(1)°. This interaction is similar to that found in bis(diethyldithiocarbamato)methylbismuth(III),[4] where sulphur bridges between symmetrically related molecules link them into dimers with slightly shorter Bi ··· S distances of 3.27 and 3.36 Å. As in compound **(1)**, the phenyl carbon, C(11), is apical with the bismuth lone pair of electrons completing the pentagonal bipyramid.

The Bi–C(11) bond length [2.241(10) Å] is similar to the corresponding length in compound **(1)**. The pattern of Bi–S bond lengths, however, differs noticeably in that the 'long' bonds are longer and the 'short' bonds are shorter. The difference between the means of the 'long' and 'short' bonds is 0.26 compared with 0.11 Å for compound **(1)**. However, the relative orientations of the long and short bonds are similar in the two structures. As might be expected, the sulphur atoms, S(2) and S(3), involved in the short Bi–S bonds, have longer S–C bonds [1.714(10) and 1.740(8) Å] than the other sulphur atoms, S(1) and S(4) [1.698(10) and 1.703(9) Å]. The S_2CNC_2 portions of both dithiocarbamato groups are planar to within ± 0.02 Å. The dihedral angles between the bismuth–phenyl plane and the S_2CNC_2 planes are 89.4(2) and 103.3(2)°. The $Bi(S_2CNC_2)_2$ grouping is planar to within ± 0.28 Å.

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