DALTON
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Solvent-free synthesis of bismuth thiolates and carboxylates

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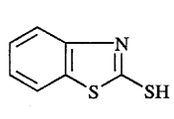
The thermally induced solvent-free reactions of Ph_3Bi with a series of thiols and carboxylic acids (2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 2-ethoxybenzoic acid, 1-mercapto-2-propanol and salicylic acid) in the ratio 1 : 3 have been investigated and shown to produce the fully substituted bismuth thiolates and benzoates in good yields and purity. Thermogravimetric analysis and differential scanning calorimetry have been used to study the profiles of those reactions involving two solid components and indicate that the reactions occur with the onset of the melting of Ph_3Bi. The two products from the reactions with 2-ethoxybenzoic acid and 1-mercapto-2-propanol have been characterised by single crystal X-ray diffraction and shown to be dimeric, $[(2\text{-}EtOC_6H_5CO_2)_3Bi]_2$, **1**, and polymeric, $[\{(CH_3CH(OH)CH_2S)(CH_3CH(O)CH_2S)\}Bi]_\infty$, **2**, respectively. Compound **1** crystallises as centro-symmetric dimers with the two Bi centres bridged by carboxylate O atoms with possible polymerisation prevented by the further interaction of one of the ethoxy groups with each metal centre. In contrast compound **2** is made up of monomeric units, containing both a mono-anion and a dianion with quasi polymeric linkages arising from bridging S atoms accompanying OH ··· O hydrogen bonding interactions between the two ligand species.

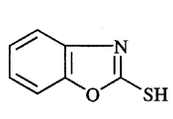
Introduction

Of all the heavy metals bismuth has the greatest potential for application within the context of green chemistry. Its compounds are less toxic than those of their lighter congeners (P, As, Sb) and are both therapeutically[1] and synthetically useful.[2–4] They are known to have a wide range of biological and medicinal uses, *e.g.* in the treatment of gastrointestinal disorders (mainly bismuth subsalicylate and subcitrate), as bactericides, fungicides, anti-parasitic agents and in prospective anti-tumour treatment.[5] One significant problem in the arena of inorganic and organometallic bismuth chemistry is the clean preparation and definitive characterisation of the compounds. Indeed many pharmaceutical preparations may still be regarded as chemically ill-defined.[5] The problem here can often be traced back to the ease with which bismuth–element bonds react with organic solvents, ligands and any water present, resulting in contamination by the partial or complete formation of oxides and hydroxides.[2,6]

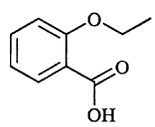
As sources of homoleptic Bi(III) compounds, L_3Bi, triarylbismuth derivatives have advantages in terms of handling and storage over the moisture-sensitive bismuth chloride, bromide, iodide or acetate. Surprisingly and advantageously, triarylbismuth compounds are less toxic than alkyl and inorganic bismuth compounds, with the LD_{50} of Ph_3Bi being 180g Kg^{-1} (dog, oral).[2] However, cleavage reactions with carboxylic acids and thiols in a range of solvents give LX_2Bi and L_2XBi compounds, often as mixtures, rather than L_3Bi.[3,7] In the case of thiols, radical initiation of cleavage may be needed.[8] In an attempt to overcome this and at the same time 'green' the reactions, we have examined reactions of Ph_3Bi with some typical aromatic carboxylic acids and thiols (below) under solventless conditions and have successfully obtained the fully substituted complexes in good yield within short reaction times. Despite the reactions being exothermic, a solvent is not necessary to act as a heat sink. Although benzene is a product of the cleavage, preliminary results indicate that Ph_3Bi can be replaced by tris-*p*-tolylbismuth giving the less toxic toluene as a by-product, a matter which remains to be explored further. The initial range of thiols and carboxylic acids we chose contained a variety of reaction sites and potential internal donor sites and are shown below. Due to the relative acidities of the thiol and alcohol groups and the consequent stability of the Bi–S bond[9] mercaptopropanol (sulfanylpropanol) was fully expected to react at –SH.



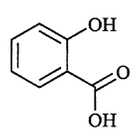
2-Mercaptobenzothiazole



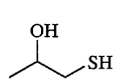
2-Mercaptobenzoxazole



2-Ethoxybenzoic acid



Salicylic Acid



1-Mercapto-2-propanol

Results and discussion

Our first attempts at solvent-free synthesis involved ball milling Ph_3Bi with the thiol or carboxylic acid in varying ratios of 1 : 1, 1 : 2 and 1 : 3 for between 1 and 12 hours. This, however, proved ultimately impractical for two reasons: (i) a complex mixture of compounds was always obtained, with the fully substituted bismuth compounds being the major isolated products, albeit in less than 40% yield and (ii) the products were always obtained as very fine powders rendering their removal and collection difficult on the scale which the reactions were conducted (typically = 10 mmol).

We then examined the simple process of heating the two components together in air. A typical experiment involved pre-mixing crystalline Ph_3Bi with the commercially available

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Table 1 Solvent-free reaction of Ph_3Bi with various thiols and carboxylic acids in a 1 : 3 ratio

Reactant	Time/h	Temperature/°C	Yield (%)	Compound colour	Mp/°C	Solubility
Mercaptobenzothiazole	3	130	97	Orange	325 (dec.)	—
Mercaptobenzoxazole	3	130	88	Mustard	260–261	—
2-Ethoxybenzoic acid	3	120	87	Colourless	147–149	Acetone, dmso
1-Mercapto-2-propanol	3	110	52	Green	144 (dec.)	—
Salicylic acid	3	130	78	Colourless	240 (dec.)	Acetone, dmso

thiol or carboxylic acid and heating the mixture slowly, without any protective atmosphere, to between 110 and 130 °C over several hours. Often there was the visible release of benzene (condensation at the neck of the vial) with an obvious transformation in the appearance of the reaction mixture, either because of solid formation or colour change. 1-Mercapto-2-propanol is a relatively low boiling point liquid (57 °C) and therefore the reaction mixture was sealed in a glass vial prior to heating. The other liquid reactant, 2-ethoxybenzoic acid, has a boiling point high enough to avoid significant loss during heating and so an open vial was adequate in this case. Again, experimentation with varying ratios of Ph_3Bi to thiol or carboxylic acid (1 : 1, 1 : 2, 1 : 3) always gave mixtures of compounds with the fully substituted bismuth thiolate or carboxylate as the main product. In the light of this we decided to limit subsequent reactions to a simple 1 : 3 ratio ($n = 3$ in Scheme 1) and target precisely the fully substituted products. The reaction conditions and yields are given in Table 1.

$$Ar_3Bi + \begin{matrix} nRSH \\ nRCOOH \end{matrix} \xrightarrow{\text{i or ii}} \begin{matrix} (RS)_nBiAr_{3-n} \\ (RCOO)_nBiAr_{3-n} \end{matrix} + nArH$$

Scheme 1 Solvent-free synthesis of bismuth thiolates and carboxylates. Conditions: (i) Ball milling, $t = 1$–12 h; (ii) heat, $T = 110$–130 °C, $t = 2$–3 h.

On cooling, the products were washed with a small amount of toluene or acetone to remove any unreacted Ph_3Bi and were then obtained in good yield. As expected all the products proved to be largely insoluble in common solvents except for $(2\text{-}EtOC_6H_4CO_2)_3Bi$, **1**, and $(2\text{-}HOC_6H_4CO_2)_3Bi$ which proved to be partially soluble in acetone from which small amounts of crystals of these compounds could be grown over several weeks. This partial solubility obviously affects the overall isolated yields which can be achieved on washing the crude product with acetone; to minimise losses the crude product can be washed several times with small amounts of toluene (3 × 5 ml) to remove the residual Ph_3Bi.

All the products were characterised by IR, elemental analysis and, where possible, by ^1H NMR and electrospray mass spectroscopy (+ and − ion). The analyses indicated that all the fully substituted compounds could be obtained in relatively high yield and in high purity. The one exception is the compound obtained from 1-mercapto-2-propanol which crystallises from an initial green oil and is difficult to recover in high yield. The crystals were identified as containing only two ligands per bismuth rather than three (see figure below) with one of the mercaptopropanol moieties being mono-anionic, $CH_3CH(OH)CH_2S^-$, and the other being a dianion, $CH_3CH(O^-)CH_2S^-$. From the stoichiometry of the reaction this leaves unreacted mercaptopropanol, which most likely accounts for the oil. When toluene or acetone is added to the oil a grey/green powder with the same composition as the crystalline product slowly precipitates.

The infra-red spectra of the crude products were useful in determining whether any unreacted Ph_3Bi remained from the reaction and, from the disappearance or otherwise of the –SH or –OH groups, which of the functional groups in the ligands had reacted and were now bonded to the bismuth centre. For example, with 2-mercaptobenzothiazole the complete absence of the –SH stretching absorption at 2500 cm^{-1} coupled with no absorptions corresponding to PhBi moieties (indicative bands 729 and 693 cm^{-1}) indicated that complete substitution had occurred. For 1-mercapto-2-propanol the IR spectrum of the crystalline product again indicated no residual Ph groups but did have a weak broad absorption at 3444 cm^{-1} corresponding to the remaining hydroxyl group. ^1H NMR spectra were obtained on the sparingly soluble products obtained from the reactions with 2-ethoxybenzoic acid and salicylic acid, and indicated traces of residual Ph groups, although these were not observable in the IR spectra. After one washing NMR indicated that purity was 95%.

To more fully understand the reaction process the reactions involving mercaptobenzothiazole, mercaptobenzoxazole and salicylic acid were investigated by TGA-DSC. These indicated the reactions proceed quickly with the onset of melting of the Ph_3Bi (mp of crystalline Ph_3Bi, 77 °C) and is consistent with the recent study of various organic 'solid/solid' reactions which required the formation of a molten phase for the reaction to proceed.[10] The TGA-DSC data for the reaction with mercaptobenzothiazole are presented in Fig. 1. As can be seen, the initial

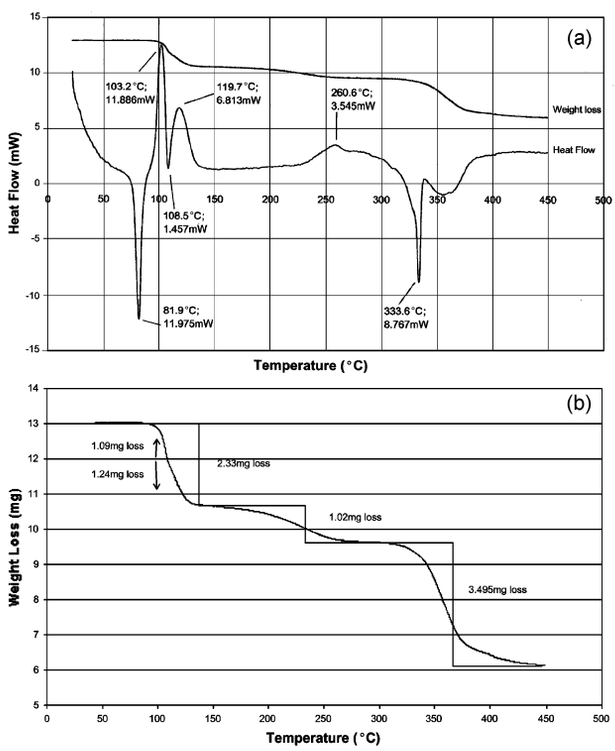

Fig. 1 (a) DSC/TGA and (b) TGA analyses of the 1 : 3 solvent-free reaction of Ph_3Bi with mercaptobenzothiazole.

endotherm corresponds with the melting of Ph_3Bi and is followed immmedately by two exothermic reactions leading to the loss of two of the Ph groups before 150 °C. The third observable weight loss, which correlates with elimination of the final equivalent of benzene, then occurs over a large temperature range of some additional 50 to 100 °C centred on 240 °C.

Given that the final product has a melting/decomposition point of 325 °C, the relatively slow rate of cleavage and reaction

Table 2 Selected bond lengths (Å) and angles (°) for $[(2\text{-}EtOC_6H_5CO_2)_3Bi]_2$, **1**. Primed atoms are related by symmetry operation $1 - x, -y, -z$

Bi–O(111)	2.325(1)	C(110)–O(111)	1.301(2)
Bi–O(112)	2.496(2)	C(110)–O(112)	1.249(2)
Bi–O(211)	2.515(2)	C(12)–O(121)	1.369(2)
Bi–O(212)	2.236(1)	C(121)–O(121)	1.464(2)
Bi–O(311)	2.207(1)	C(210)–O(211)	1.252(2)
Bi–O(312)	2.532(1)	C(210)–O(212)	1.293(3)
Bi–O(111′)	2.758(1)	C(310)–O(311)	1.293(2)
Bi–O(121′)	3.023(1)	C(310)–O(312)	1.256(3)
O(111)–Bi–O(112)	54.22(4)	Bi–O(111)–Bi′	108.07(5)
O(211)–Bi–O(212)	54.85(5)	O(111)–C(110)–O(112)	119.5(2)
O(311)–Bi–O(312)	55.06(4)	O(211)–C(210)–O(212)	119.9(2)
O(111)–Bi–O(211)	129.32(5)	O(311)–C(310)–O(312)	120.2(2)
O(111)–Bi–O(311)	81.53(5)	O(111)–Bi–O(111′)	71.93(4)
O(211)–Bi–O(311)	76.41(6)	O(211)–Bi–O(121′)	69.32(5)
O(111)–Bi–O(121′)	128.87(4)	O(311)–Bi–O(121′)	144.15(5)

of the third Ph group could be simply a transport effect. Consistent with this, bulk syntheses are achieved at 110–130 °C with reaction times of only 2–3 h. We are currently investigating the possibility of using microwave radiation to shorten reaction times by rapid heating to *ca.* 250 °C. Full decomposition does not occur until the temperature reaches *ca.* 350 °C. In contrast the TGA-DSC analysis of the reaction with mercaptobenzoxazole indicated that Ph_3Bi loses all three Ph groups within a temperature range of 90–120 °C. One reason for this difference could be that the reaction with mercaptobenzoxazole is much more kinetically favourable than for mercaptobenzothiazole if we assume that Bi–C bond cleavage and deprotonation of the thiol group is preceded by coordination of either or both chalcogenide atoms to the bismuth centre. Given that O might be expected to coordinate more strongly than S then the ability of the oxazole to bind to a crowded Bi centre would be greater than for the thiazole leading to a more facile elimination of the final Ph group.

A similar situation to mercaptobenzothiazole is observed with salicylic acid in that a weight loss corresponding to disubstitution occurs quickly (*ca.* 80–110 °C) with the loss of the final equivalent of benzene occurring over a larger temperature range, from 150–200 °C. Melting and decomposition then occurs from *ca.* 230 °C onwards. This may explain why with salicylic acid we were initially unable to consistently obtain a high purity product, since over the prolonged heating period there is most likely coincident product formation and decomposition. Again rapid heating to 200 °C by microwave radiation and cooling quickly may alleviate this problem.

The reactions of 2-ethoxybenzoic acid and 2-mercaptobenzothiazole were also conducted with tris-*p*-tolylbismuth in replacement of Ph_3Bi. The co-product is then the less toxic toluene, which could be easily recovered through condensation and collection. The melting point of crystalline tris-*p*-tolylbismuth is higher than that of Ph_3Bi (118 °C *vs.* 77 °C) and therefore the reaction mixtures were heated to higher temperatures (140–150 °C) to facilitate both the melting of tris-*p*-tolylbismuth and the removal of toluene. Both reactions gave products identical to those obtained with Ph_3Bi, providing the basis for future study and greener syntheses.

Single crystal X-ray diffraction studies

Three of the compounds were obtained as crystalline materials, either from the reaction mixture (2-mercaptopropanol) or from acetone (2-ethoxybenzoic acid and salicylic acid). Unfortunately, the crystals of bismuth tris-salicylate were consistently twinned and to-date this has prevented solution of the solid state structure. However, data measured on the other two samples allowed for solution of the crystal structures. $[(2\text{-}EtOC_6H_5CO_2)_3Bi]_2$, **1**, crystallises in the triclinic space group $P\bar{1}$ with one centrosymmetric binuclear molecule in the unit cell and is only the second structural characterisation of a bismuth benzoate. The structure is shown in Fig. 2 and reveals that two

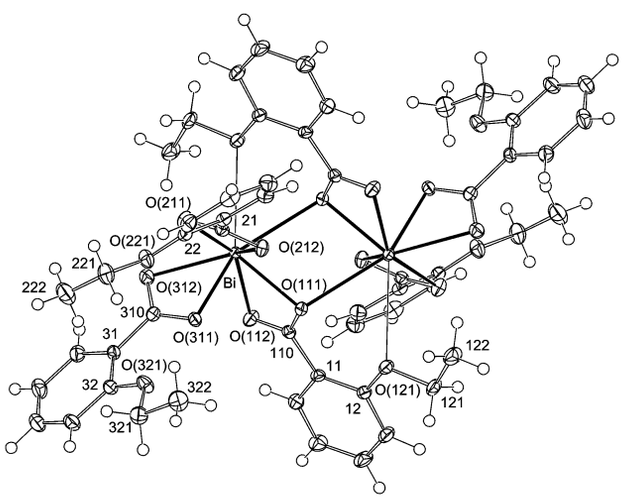

Fig. 2 Molecular structure of $[(2\text{-}EtOC_6H_5CO_2)_3Bi]_2$, **1**.

$(2\text{-}EtOC_6H_5CO_2)_3Bi$ monomers are joined by bridging O atoms from carboxylate moieties which are coordinated in the less usual bridging tridentate manner, giving overall eight-coordinate Bi. Selected bond lengths and angles for **1** are given in Table 2. The gross structural features are similar to those described previously for polymeric bismuth tribenzoate itself, $[(C_6H_4CO_2^-)_3Bi]_\infty$,[11] which also has tridentate carboxylate bridges. In fact the majority of crystallographically characterised bismuth carboxylates are polymeric, primarily due to the ability of Bi to attain a high coordination environment, and the ease with which the carboxylates bridge Bi centres.[2] However, in the case of **1** polymerisation of the dinuclear unit is blocked by the coordination of the O atoms in the ethoxy side arms of the bridging ligands with each metal centre. These long Bi–O*Et* interactions obviously occupy a vacant coordination site which in bismuth tribenzoate allows for a second bridging carboxylate group and hence growth of the one-dimensional polymeric structure. The range of Bi–O distances in **1** is 2.207(1) (Bi–O(311)) to 3.023(1) Å (Bi–O121′)), with the latter being the longer Bi–O*Et* bond. Each carboxylate group forms one short and one longer bond to the bismuth centre with the $-CO_2^-$ group which forms the bridge between the two bismuth centres revealing a slight elongation in the short bond distance (2.325(1) *vs.* 2.236(1) and 2.207(1) Å) as that particular O centre compensates for binding to a second Bi centre (distance 2.758(1) Å). It is these longer bonds which participate in the central planar four-membered $(BiO)_2$ ring relative to which the ethoxybenzoate moieties associated with each Bi largely occupy a transoid position with the 'free' space accommodating the lone pair on the Bi atom, as shown in Fig. 2. An analysis of the bond angles formed by the Bi–O bonds around the Bi centre indicates that the arrangement is not symmetrical.

The structure derived from 1-mercapto-2-propanol, [{(CH_3-$CH(OH)CH_2S)(CH_3CH(O)CH_2S)$}Bi]$_\infty$, **2**, can be compared with those described for 2-mercaptoethanolatobismuth(III), the various complexes of which have been shown to be highly active against *Heliobacter pylori* and the urease which it produces.[12,13] The crystal structure of **2** is shown in Fig. 3 while a comparison

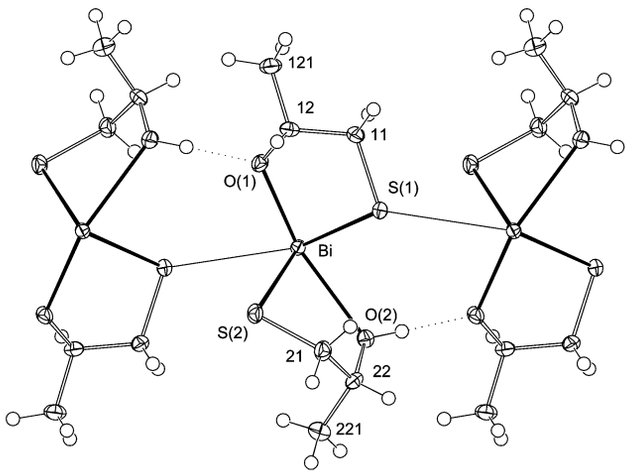

Fig. 3 Structure of [{$(CH_3CH(OH)CH_2S)(CH_3CH(O)CH_2S)$}Bi]$_\infty$, **2**.

with the analogous 2-mercaptoethanolato complex, **3**, is shown in Fig. 4.[12] Bond lengths and angles for **2** are given in Table 3.

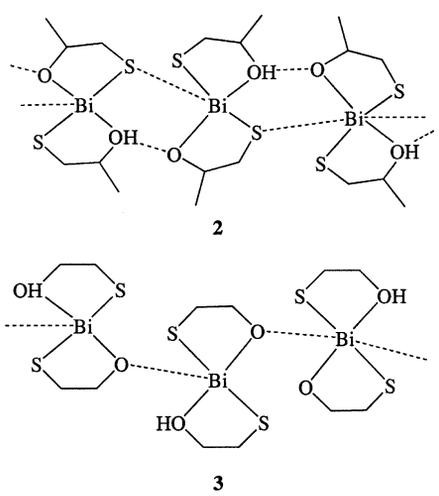

Fig. 4 Comparison of the bonding modes within the polymers **2** and **3**.

As can be seen, while both complexes contain bidentate ligands the one-dimensional association of monomers in **2** is formed on the basis of both Bi–S linkages and hydrogen bonding between the OH group (the H of which was located and refined) and the neighbouring alkoxo O atom (*av.* 1.8 Å) while **3** is constructed solely from Bi–O linkages. The Bi–S bonds in both complexes, though, are comparable, 2.582(1), 2.560(1)Å in **2** and 2.527(3), 2.564(3)Å in **3**, with the bond which connects the 'monomer' units in **2** being significantly longer at 3.262(1)Å, though well within the range expected of bridging Bi–S bonds. The Bi–O bonds are essentially identical, 2.197(4), 2.589(4) Å in **2** and 2.195(9), 2.577(9) in **3**. The molecules shown in **2** are in the *R* configuration though the crystals themselves are centrosymmetric and therefore racemic, *i.e.* contain both *R* and *S* forms.

Three other complexes derived from 2-mercaptoethanol have been previously structurally characterised[12] and are simply thiolates of type $(RS)_2BiX$ in which the ligand acts in a bidentate manner and X = NO_3^-, Cl^- and $MeCO_2^-$. Thiolato bridging occurs only in the nitrate complex (bond distances 2.853(6)–2.959(8) Å) allowing formation of a polymeric structure *via* a series of connected $(BiS)_2$ rings.

Table 3 Bond lengths (Å) and angles (°) for [{$(CH_3CH(OH)CH_2S)$-$(CH_3CH(O)CH_2S)$}Bi]$_\infty$, **2**. Primed and double primed atoms are related by the symmetry operations $1 - x$, $y - 1/2$, $1/2 - z$ and $1 - x$, $1/2 + y$, $1/2 - z$

Bi–S(1)	2.582(1)	S(2)–C(21)	1.830(6)
Bi–O(1)	2.197(4)	O(2)–C(22)	1.440(7)
Bi–S(2)	2.560(1)	C(11)–C(12)	1.519(7)
Bi–O(2)	2.589(4)	C(12)–C(121)	1.511(8)
Bi–S(1′)	3.262(1)	C(21)–C(22)	1.529(8)
S(1)–C(11)	1.815(1)	C(22)–C(221)	1.512(3)
O(1)–C(12)	1.426(1)	O(2)–H	1.0(1)
S(1)–Bi–O(1)	80.3(1)	Bi–O(1)–C(12)	118.6(3)
S(1)–Bi–S(2)	92.14(4)	Bi–S(2)–C(21)	97.9(2)
S(1)–Bi–O(2)	78.86(9)	Bi–O(2)–C(22)	117.3(3)
S(1)–Bi–S(1′)	156.83(4)	C(11)–S(1)–Bi″	114.0(2)
O(1)–Bi–S(2)	99.5(1)	S(1)–C(11)–C(12)	112.2(4)
O(1)–Bi–O(2)	158.0(1)	O(1)–C(12)–C(11)	111.7(4)
O(1)–Bi–S(1′)	81.0(1)	O(1)–C(12)–C(121)	108.9(4)
S(2)–Bi–O(2)	74.21(9)	C(11)–C(12)–C(121)	110.8(4)
S(2)–Bi–S(1′)	77.63(4)	S(2)–C(21)–C(22)	113.8(4)
O(2)–Bi–S(1′)	117.15(9)	O(2)–C(22)–C(21)	109.5(4)
Bi–S(1)–C(11)	93.4(2)	O(2)–C(22)–C(221)	109.1(5)
Bi–S(1)–Bi″	115.85(5)	C(21)–C(22)–C(221)	112.6(5)

Conclusion

We have established that the use of Ph_3Bi in a stoichiometric 1 : 3 reaction with carboxylic acids and thiols can provide a solvent-free process for synthesising bismuth thiolates and carboxylates through heating at relatively low temperatures. The products can be obtained in relatively high yields and of significantly high purity. TGA-DSC analysis indicated the onset of Ph substitution occurs rapidly on reaching the melting point of Ph_3Bi. Initial studies with tris-*p*-tolylbismuth indicates that this would be an appropriate alternative to the use of Ph_3Bi, although further studies in this area are warranted.

Experimental

Ph_3Bi, previously obtained from Walman International, was recrystallised from toluene and the purity checked by NMR and mass spectroscopy. 2-Mercaptobenzothiazole (98%) and salicylic acid (99%) were from Merck-Schuchardt while 2-mercaptobenzoxazole (95%), 2-ethoxybenzoic acid (98%), 1-mercapto-2-propanol (95%, racemic mixture), were from Aldrich. All reagents were used without further purification. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted using a STA1500 instrument (Rheometric Scientific) in a nitrogen atmosphere (50 ml min^{-1}) between 30 and 400 °C with a temperature ramp rate of 10 ° min^{-1}. The instrument was calibrated using four melting points (indium, tin, lead, zinc) and aluminium pans were used in all experiments. Infra-red spectra were obtained on a Perkin-Elmer 1600 FTIR. NMR spectra were obtained with a Bruker DRX-400 spectrometer with chemical shifts referenced to the appropriate deuteriated solvent. Elemental analyses were carried out by CMAS, Melbourne, Australia.

X-Ray diffraction

Full spheres of low-temperature CCD area-detector diffractometer data were measured (Bruker AXS instrument, ω-scans; monochromatic MoK_α radiation, ($\lambda = 0.7107_3$ Å), $2\theta_{max} = 75°$; *T ca.* 153 K, yielding $N_{t(otal)}$ reflections, merging after 'empirical'/multiscan absorption correction (proprietary software) to *N* unique (R_{int} quoted), N_o with $F > 4\sigma(F)$ considered 'observed' and used in the full matrix least squares refinement (anisotropic thermal parameter forms for Bi,S,O,C, $(x, y, z, U_{iso})_H$ constrained at estimates). Conventional residuals *R*, R_w on |*F*| are cited; neutral atom complex scattering factors were employed

within the Xtal 3.7 program system.[14] Pertinent results are given below and in the tables and figures, the latter showing 50% probability amplitude displacement envelopes for Bi,S,O,C, hydrogen atoms having arbitrary radii of 0.1 Å.

Crystal/refinement data. 1. $C_{54}H_{54}Bi_2O_{18}$, M = 1409.0, triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a = 10.5533(9), b = 11.3356(10), c = 12.3665(10) Å, α = 87.561(2), β = 71.084(2), γ = 67.110(2)°, V = 1283 Å^3. D_c (Z = 1 dimer) = 1.82$_3$ g cm^{-3}. μ_{Mo} = 69 cm^{-1}; specimen: 0.13 × 0.12 × 0.10 mm; 'T'$_{min,max}$ = 0.63, 0.80. N_t = 26703, N = 13184 (R_{int} = 0.031), N_o = 11101; R = 0.024, R_w = 0.019.

2: $C_6H_{13}BiO_2S_2$, M = 390.3, orthorhombic, space group *Pbca* (D_{2h}^{15}, No. 61), a = 9.4779(8), b = 9.8471(8), c = 21.152(2) Å, V = 1974 Å^3. D_c (Z = 8) = 2.62$_6$ g cm^{-3}. μ_{Mo} = 182 cm^{-1}; specimen: 0.10 × 0.06 × 0.03 mm; 'T'$_{min,max}$ = 0.43, 0.83. N_t = 41184, N = 5117 (R_{int} = 0.078), N_o = 3128; R = 0.034, R_w = 0.031.

Variata. The hydroxylic hydrogen was secured by refinement.

CCDC reference numbers 191117 and 191118.

See http://www.rsc.org/suppdata/dt/b2/b209347b/ for crystallographic data in CIF or other electronic format.

Syntheses

General procedure. All reactions were conducted using 2.5 mmol of Ph_3Bi and 7.5 mmol of thiol or carboxylic acid. Crystalline Ph_3Bi was mixed with the carboxylic acid or thiol and the mixture of reagents placed in a glass vial and heated in an oil bath to between 110 and 130 °C for 2–3 h. If the reactants were both solids they were ground together prior to heating. For the low boiling point liquid, 1-mercapto-2-propanol, the glass vial was sealed to prevent losses through evaporation. For the reactions with two solid components the mixture became liquid at the onset of melting of the Ph_3Bi (80–90 °C) at which point the reaction commenced. A colourless liquid (benzene) was seen to condense at the top of the glass vial. On cooling, the solid products were washed with acetone and/or toluene and dried over anhydrous $CaCl_2$ in a vacuum desiccator prior to any analysis. Variations for each reaction are given below.

1 : 3 Reaction of Ph_3Bi with 2-mercaptobenzothiazole. Reaction at 130 °C for 2 h produced a bright orange solid, which is insoluble in a range of common solvents. Yield 97% (1.72 g), mp 325 °C (dec.), IR (Nujol, cm^{-1}) 1497w, 1428s, 1377m, 1320m, 1312m, 1277w, 1243m, 1077m, 1024s, 1010s, 1000s, 750s, 722m, 708w, 680m. Elemental analysis; ($C_{21}H_{12}N_3S_6Bi$), Calc (Found): C 35.6 (35.6), H 1.7 (1.7), N 5.7 (5.8), S 27.2 (27.1)%.

1 : 3 Reaction of Ph_3Bi with 2-mercaptobenzoxazole. Reaction at 130 °C for 3 h produced a mustard coloured solid, which is insoluble in a range of common solvents. Yield 88% (1.45g), mp 260–261 °C (dec.). IR (Nujol, cm^{-1}) 2361w, 1595w, 1474s, 1461s, 1376m, 1336w, 1282w, 1245s, 1225m, 1174w, 1150m, 1138s, 1127s, 1095m, 1001w, 927w, 939w, 890w, 843w, 805m, 738s, 668w. Elemental analysis; ($C_{21}H_{12}N_3S_3O_3Bi$), Calc (Found): C 38.2 (38.1), H 1.8 (1.8), O 7.3 (7.4), N 6.4 (6.3), S 14.6 (14.6)%.

1 : 3 Reaction of Ph_3Bi with 2-ethoxybenzoic acid. The liquid reaction mixture was heated at 120 °C for 3 h resulting in a gel-like solid. Addition of a small amount of acetone to the hot mixture results in precipitation of a white powder, which is slightly soluble in a larger excess of acetone. The washed product was recrystallised from acetone over 2 w to give large prismatic colourless crystals of tris-2-ethoxybenzoatobismuth, [(2-$EtOC_6H_4CO_2^-$)$_3$Bi]$_2$. Yield 87% (1.53 g) mp 147–149 °C. IR (Nujol, cm^{-1}) 3117vw, 3082vw, 1728vw, 1601s, 1582s, 1540s, 1522s, 1500m, 1477m, 1377s, 1353s, 1286m, 1276m, 1252s, 1225m, 1179m, 1162m, 1152m, 1117m, 1099w, 1043m, 928w, 914w, 865m, 857m, 790w, 759s, 751s, 719w, 706m, 674m. Elemental analysis; ($C_{54}H_{54}O_{18}Bi_2$) Calc (Found): C 46.0 (45.9), H 3.8 (3.8). ^{1}H NMR (400 MHz, d$_8$-acetone, 30 °C) δ 7.62 (d, 6H, 6 × CH, J = 6.9 Hz); 7.41 (br, 6H, 6 × CH); 7.07 (br, 6H, 6 × CH) 6.95 (br, 6H, 6 × CH); 4.05 (q, 12H, 6 × CH_2, J = 6.3 Hz); 1.27 (br, 3H, CH_3). Mass spectrum; ES$^+$: 727 (L_3BiNa^+); 597 (L_2Bi·acetone$^+$); 539 (L_2Bi^+), ES$^-$: 869 (L_4Bi^-); 165 (L^-).

1 : 3 Reaction of Ph_3Bi with 1-mercapto-2-propanol. Liquid reaction mixture heated to 110 °C for 2 h producing a green oil which on removal and storage over a period of one week produced a moderate crop of green crystals. The oil was not miscible with toluene and the addition of acetone caused precipitation of a grey/green powder which was analytically consistent with the crystalline product. Yield 52% (0.51g), mp 144–145 °C (dec.). Elemental analysis; ($C_6H_{13}O_2S_2Bi$), Calc (Found): C 18.5 (18.8), H 3.3 (3.4), O 8.2 (7.8), S 16.4 (16.5)%. IR (Nujol, cm^{-1}) 3444w, 2590m br, 1962m, 1726w (br), 1606w, 1459s, 1413m, 1376m, 1319m, 1311m, 1240m, 1222w, 1185m, 1113m, 1071m, 1049m, 1023s, 930m, 895w, 871w, 836w, 737w, 697w.

1 : 3 Reaction of Ph_3Bi with salicylic acid. Reaction mixture heated to 130 °C for 3 h producing a white coloured solid which on cooling was washed with toluene and acetone. Recrystallisation from acetone produced some colourless crystals, which unfortunately were unsuitable for single crystal X-ray studies. Yield before recrystallisation 78% (1.21 g), mp 240 °C (dec.). Elemental analysis; ($C_{21}H_{15}O_9Bi$) Calc (Found): C 40.6 (40.8), H 2.4 (2.3)%. IR (Nujol, cm^{-1}) 3286m, 3100w, 3040w, 1620s, 1587m, 1524s, 1483s, 1464s, 1437s, 1399m, 1379s, 1308m, 1253s, 1223m, 1159m, 1143m, 1055w, 1031w, 996w, 872m, 817m, 763m, 753s, 732s, 702m, 692m, 670s, 646m (sh). ^{1}H NMR (300 MHz, d$_8$-acetone, 30 °C) δ 7.80 (d, 3H, 3 × CH, J = 7.8 Hz); 7.16 (d, 3H, 3 × CH, J = 7.8 Hz) 6.65 (br, 3H, 3 × CH); 6.50 (t, 3H, 3 × CH, J = 7.2 Hz); OH not observed.

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