Chalcogenolato Complexes of Bismuth and Antimony. Syntheses, Thermolysis Reactions, and Crystal Structure of $Sb(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3$†

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Antimony(III) and bismuth(III) complexes of sterically demanding arenechalcogenolato ligands, $M(EC_6H_2R'_3\text{-}2,4,6)_3$ (E = S or Se; M = Sb or Bi; R′ = Me, Pr^i or Bu^t) have been prepared by either protolysis of the amides $M[N(SiMe_3)_2]_3$ with arenechalcogenols, or from MCl_3 by halide exchange (M = Bi or Sb). The complexes are monomeric in the solid state and sublime readily. The crystal structure of $Sb(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3$ has been determined by X-ray diffraction. The compound possesses a trigonal-pyramidal geometry, with Sb–S distances of 2.418(2)–2.438(2) Å and S–Sb–S angles of 94.69(7)–98.29(8)°. Preliminary X-ray results on $Bi(SeC_6H_2Pr^i{}_3\text{-}2,4,6)_3$ showed that the compounds of Sb and Bi are isostructural. Thermolytic decomposition of some of the compounds has been carried out in the solid state. Compounds with R′ = Me or Pr^i undergo reductive elimination to give elemental bismuth or antimony, whereas the bulky selenolates $M(SeC_6H_2Bu^t{}_3\text{-}2,4,6)_3$ afford M_2Se_3.

Bismuth and antimony chalcogenides are currently of interest due to their growing importance for material applications such as their use as semiconductors, as optical data-storage media, thermoelectric materials, capacitors and intercalatable battery cathodes.[1] As an expansion of our studies on Group 12[2] and transition-metal[3] chalcogenolato complexes as single-source precursors for the deposition of solid-state metal chalcogenide materials, we report here the synthesis and characterisation of a series of homoleptic chalcogenolato complexes of bismuth and antimony. While various bismuth and antimony thiolates have been studied,[4] there are only few examples of corresponding selenolato and tellurolato complexes. The present investigation was undertaken in order to test the suitability of arenechalcogenolato compounds as single-source precursors for the preparation of Group 15 chalcogenide solid-state materials.

Results and Discussion

Chalcogenolato complexes of antimony and bismuth are generally accessible *via* two alternative methods [equations (1) and (2); R = aryl, E = S or Se]. The protolysis of metal amides

$$M[N(SiMe_3)_2]_3 + 3REH \longrightarrow M(ER)_3 + 3NH(SiMe_3)_2 \quad (1)$$

$$MCl_3 + 3LiER \longrightarrow M(ER)_3 + 3LiCl \quad (2)$$

with the corresponding chalcogenols [method A, equation (1)][2] has the advantage of yielding compounds free of ionic impurities under very mild conditions. The ligands employed are $2,4,6\text{-}Me_3C_6H_2E^-$ (R^1E^-), $2,4,6\text{-}Pr^i{}_3C_6H_2E^-$ (R^2E^-) and $2,4,6\text{-}Bu^t{}_3C_6H_2E^-$ (R^3E^-).

Thiolato Complexes.—The reaction of 2,4,6-trimethylbenzenethiol (R^1SH) with $M[N(SiMe_3)_2]_3$ (M = Bi or Sb) in light petroleum or $LiSR^1$ and MCl_3 in tetrahydrofuran (thf) leads to the formation of $Bi(SR^1)_3$ **1** and $Sb(SR^1)_3$ **2** as yellow and white crystals, respectively. The analogous protolysis of the bismuth or antimony amido complexes using the sterically more hindered tris(isopropyl)benzenethiol (R^2SH) and tris(*tert*-butyl)benzenethiol (R^3SH) gives the corresponding metal thiolato complexes in high yields (Table 1). The thiolates show good solubility in common organic solvents and are air-stable in the solid state for prolonged periods. Solutions are however prone to oxidation with formation of the corresponding diaryl disulfides. The complexes sublime readily at elevated temperatures under reduced pressure. The monomeric nature of these compounds in the solid state is confirmed by the crystal structure of $Sb(SR^1)_3$ (Fig. 1) The NMR data for the new compounds are collected in Table 2.

Selenolato Complexes.—The complexes were prepared according to either equation (1) or (2) as yellow to red crystalline solids which resemble the thiolates in their physical properties; they possess good solubility in common organic solvents, are air-stable in the solid state and sublime at moderate temperatures. They are best recrystallised from relatively polar solvents, such as acetonitrile–ethyl acetate mixtures.

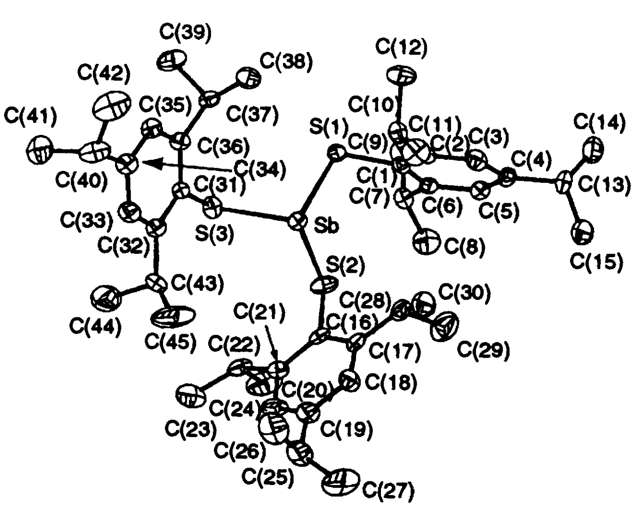

Fig. 1 Molecular structure of $Sb(SC_6H_2Pr^i{}_3\text{-}2,4,6)_3$ **6**, showing the atomic numbering scheme. Ellipsoids correspond to 30% probability

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue, 1, pp. xxv–xxx.

Non-SI unit employed: bar = 10^5 Pa.

Table 1 Analytical and physical data for the complexes

Complex		Colour	Yield (%)[a]	M.p./°C	Analysis[b] (%)		
					C	H	S
1	$Bi(SR^1)_3$	Yellow	86	142–144	48.9 (48.7)	5.0 (4.9)	14.5 (14.4)
2	$Sb(SR^1)_3$	White	75	80[c]	56.4 (56.4)	5.7 (5.7)	16.7 (16.6)
3	$Bi(SeR^1)_3$	Yellow	68	116[c]	40.4 (39.9)	4.1 (4.2)	
4	$Sb(SeR^1)_3$	Pale yellow	69	78	45.3 (45.2)	4.6 (4.6)	
5	$Bi(SR^2)_3$	Orange	85	102–104	59.1 (59.1)	7.6 (7.8)	10.1 (10.1)
6	$Sb(SR^2)_3$	White	89	94–95	65.3 (65.1)	8.3 (8.6)	11.6 (11.5)
7	$Bi(SeR^2)_3$	Red	87	122–124	51.2 (51.1)	6.5 (6.5)	
8	$Sb(SeR^2)_3$	Yellow	89	90–92	55.8 (56.9)	7.1 (7.4)	
9	$Bi(SR^3)_3$	Orange	86	166–168	62.3 (61.0)	8.4 (8.3)	9.3 (9.2)
10	$Sb(SR^3)_3$	Yellow	82	206[c]	68.0 (68.8)	9.1 (9.2)	10.1 (9.8)
11	$Bi(SeR^3)_3$	Red	87	150[c]	54.9 (53.9)	7.4 (7.5)	
12	$Sb(SeR^3)_3$	Yellow	76	185–187	59.2 (59.7)	8.0 (8.0)	

[a] Based on method A. [b] Required values given in parentheses. [c] With decomposition.

Table 2 Proton and ^{13}C NMR data for antimony and bismuth chalcogenolates

Compound	^{1}H NMR[a]	^{13}C NMR[a]
1	2.44 (s, 3 H, *p*-Me), 2.52 (s, 6 H, *o*-Me), 7.0 (s, 2 H, aryl)[b]	144.1, 138.3, 128.3, 23.2, 20.6[b]
2	2.26 (s, 3 H, *p*-Me), 2.38 (s, 6 H, *o*-Me), 6.9 (s, 2 H, aryl)[b]	143.2, 137.6, 129.1, 127.1, 23.3, 20.9[c]
3	2.34 (s, 3 H, *p*-Me), 2.45 (s, 6 H, *o*-Me), 6.9 (s, 2 H, aryl)[b]	144.5, 138.5, 128.2, 125.7, 25.8, 20.6[c]
4	2.23 (s, 3 H, *p*-Me), 2.40 (s, 6 H, *o*-Me), 6.87 (s, 2 H, aryl)[b]	143.6, 137.9, 128.3, 126.5, 25.8, 24.1, 20.8[c]
5	1.15 (d, 6 H, J = 6.8, $\mathrm{CH}Me_2$), 1.26 (d, 12 H, J = 6.8, $\mathrm{CH}Me_2$), 2.95 (spt, 1 H, J = 6.8, $\mathrm{C}H\mathrm{Me}_2$), 3.81 (spt, 2 H, J = 6.8, $\mathrm{C}H\mathrm{Me}_2$), 7.02 (s, 2 H, aryl)[b]	154.9, 149.9, 128.5, 121.1, 34.4, 32.5, 24.7, 24.5[b]
6	1.12 (d, 6 H, J = 6.8, $\mathrm{CH}Me_2$), 1.22 (d, 12 H, J = 6.8, $\mathrm{CH}Me_2$), 2.85 (spt, 1 H, J = 6.8, $\mathrm{C}H\mathrm{Me}_2$), 3.78 (spt, 2 H, J = 6.8, $\mathrm{C}H\mathrm{Me}_2$), 6.97 (s, 2 H, aryl)[b]	153.2, 148.8, 125.8, 121.7, 34.3, 32.2, 24.0[b]
7	1.16 (d, 6 H, J = 7.0, $\mathrm{CH}Me_2$), 1.26 (d, 12 H, J = 7.0, $\mathrm{CH}Me_2$), 2.94 (spt, 1 H, J = 7.0, $\mathrm{C}H\mathrm{Me}_2$), 3.80 (spt, 2 H, J = 7.0, $\mathrm{C}H\mathrm{Me}_2$), 7.00 (s, 2 H, aryl)[b]	154.4, 149.7, 124.8, 121.1, 34.8, 34.0, 24.5, 24.2[c]
8	1.15, (d, 6 H, J = 6.8, $\mathrm{CH}Me_2$), 1.25, (d, 12 H, J = 6.8, $\mathrm{CH}Me_2$), 2.88, (spt, 1 H, J = 6.8, $\mathrm{C}H\mathrm{Me}_2$), 3.79, (spt, 2 H, J = 6.8, $\mathrm{C}H\mathrm{Me}_2$), 7.00 (s, 2 H, aryl)[b]	153.5, 149.1, 121.2, 34.9, 34.2, 24.2, 23.9[d]
9	1.29 (s, 9 H), 1.49 (s, 18 H), 7.37 (s, 2 H)[b]	157.0, 149.8, 127.5, 121.3, 38.1, 34.5, 33.2, 31.7[b]
10	1.30 (s, 9 H), 1.47 (s, 18 H), 7.29 (s, 2 H)[c]	155.3, 148.4, 127.6, 122.5, 38.3, 34.8, 33.2, 31.4[c]
11	1.32 (s, 9 H, *o*-Me), 1.63 (s, 18 H, *p*-Me), 7.40 (s, 2 H, aryl)[c]	156.2, 149.1, 122.9, 121.3, 38.9, 34.7, 33.1, 31.5[c]
12	1.29, (s, 9 H), 1.52, (s, 18 H), 7.31, (s, 2 H)[c]	155.9, 148.9, 123.2, 122.3, 39.1, 34.8, 33.2, 31.2[c]

[a] In $CDCl_3$ at room temperature, J/Hz. [b] At 90 MHz. [c] At 270 MHz. [d] One aryl C obscured by another peak.

Table 3 Thermal decomposition of chalcogenolato compounds of Sb and Bi

Compound	10^6 Reactor pressure/ mbar	T/°C	Inorganic residue[a]	Main organic by-product[b]
1	6.0	200	Bi	$R^1{}_2S_2$
3	5.0	200	Bi	$R^1{}_2Se_2$
4	2.5	250	Sb	$R^1{}_2Se_2$
9	6.0	170	Bi	$R^3{}_2S_2$
	7.0	200	Bi	$R^3{}_2S_2$
	5.0	250	Bi	$R^3{}_2S_2$
10	2.5	250	*c*	*c*
11	1.6	200	$Bi + Bi_2Se_3$	$R^3{}_2Se_2$
12	1.5	200	Sb_2Se_3	$R^3{}_2Se_2$

[a] As determined by powder X-ray diffraction. [b] By mass spectrometry. [c] No decomposition observed below 350 °C.

Attempted Synthesis of Tellurolato Complexes.—Attempts to obtain bismuth or antimony tellurolato complexes $M(TeC_6H_2R'_3\text{-}2,4,6)_3$ (R′ = Me, Pr^i or Bu^t) were generally unsuccessful. In some cases the formation of the tellurolato complexes was observed at low temperatures; however, decomposition took place on warming to room temperature, and only diaryl ditellurides and tellurium powder were recovered. Evidently arenetellurolato compounds of bismuth and antimony undergo facile reductive elimination and are thermally unstable.

Thermolysis Reaction Products.—Bismuth chalcogenides are widely used as laser-sensitive optical recording media, especially the selenides and tellurides.[1] We have investigated the behaviour of some of the new bismuth and antimony compounds under thermolysis conditions at low pressure. The results are summarised in Table 3. Thermolyses of most of compounds **1**, **3**, **4** and **9** under the conditions given in the Table results in the formation of elemental bismuth and antimony, respectively, and organic by-products, mainly the diaryl dichalcogenides. Powder X-ray diffraction (XRPD) provided no evidence for the formation of metal chalcogenides, even at lower decomposition temperatures. Evidently the Bi–E bonds rupture under these conditions in preference to the E–C bonds, in contrast to the behaviour of Group 12 metal chalcogenides.[2] Elemental selenium was not observed in the XRPD spectra. The compound $Sb(SR^3)_3$ **10** is thermally unexpectedly stable and does not decompose below 350 °C, whereas the analogous bismuth compound **9** deposits elemental Bi at 200 °C, no doubt a reflection of the lower Bi–S bond strength in diatomic molecules:[5] Bi–S 75.4 ± 1.1, Sb–S 90.5, and Bi–Se 67.0 ± 1.4 kJ mol^{-1}.

By contrast to the compounds mentioned above, the bulky selenolato complex $Sb(SeR^3)_3$ **12** decomposes at 200 °C to give antimony selenide, Sb_2Se_3. Similarly, $Bi(SeR^3)_3$ **11** gives a mixture of elemental bismuth and Bi_2Se_3. The decomposition to give Sb or Bi is accompanied by the formation of R_2E_2, while

Table 4 Selected bond distances (Å) and angles (°) for compound **6**

Sb–S(1)	2.438(2)	Sb–S(2)	2.418(2)
Sb–S(3)	2.420(2)	C(1)–S(1)	1.784(8)
C(16)–S(2)	1.816(7)	C(31)–S(3)	1.802(6)
S(2)–Sb–S(1)	94.69(7)	S(3)–Sb–S(1)	95.12(7)
S(3)–Sb–S(2)	98.29(8)	C(1)–S(1)–Sb	100.7(2)
C(16)–S(2)–Sb	94.3(2)	C(31)–S(3)–Sb	99.4(2)
C(2)–C(1)–S(1)	122.2(7)	C(6)–C(1)–S(1)	117.9(6)
C(17)–C(16)–S(2)	121.3(7)	C(21)–C(16)–S(2)	116.6(7)
C(36)–C(31)–S(3)	119.6(5)	C(32)–C(31)–S(3)	119.1(6)

in the cases of **11** and **12** the diaryl monoselenide, $R^3{}_2Se$, is observed.

Structures of $Sb(SR^2)_3$ **6** *and* $Bi(SeR^2)_3$ **7**.—Colourless crystals of compound **6** were found suitable for X-ray diffraction. The structure is shown in Fig. 1. Selected bonding parameters are collected in Table 4. The crystal of the bismuth compound and the intensity data were of poor quality, and the *R* factor could not be reduced below 0.09. A preliminary structure determination confirmed, however, that the two compounds have analogous molecular geometries.* Only the structure of **6** is discussed here in detail. While this work was in progress, the independent synthesis and structure of $Bi(SR^3)_3$ **9** was reported.[6]

As shown in Fig. 1, each antimony in the monomeric molecule is surrounded by three sulfur atoms in a trigonal-pyramidal arrangement (angle sum around Sb: 288.1°). The Sb–S bond lengths range from 2.418(2) to 2.438(2) Å. There are few examples of structurally characterised antimony and bismuth thiolato compounds. In the S–N chelate compounds $Sb(2\text{-}SC_5H_4N)_3$ and $Sb[2\text{-}SC_5H_3N(SiMe_3)\text{-}6]_3$ the central atom is six-co-ordinate, with average Sb–S distances of 2.47 and 2.488 Å, respectively, slightly longer than in **6**, while the sums of the S–Sb–S angles are smaller, close to 270°.[7] Similar variations in Sb–S bond lengths, from 2.416 to 2.55 Å, are also a feature of solid-state compounds such as $RbSb_3S_5$ and MSb_4S_7 (M = K_2 or Sr).[8]

The structure of compound **6** contains no unusually close intermolecular contacts, and although bulky arenechalcogenolato ligands are often used in order to provide steric hindrance, there is no evidence for such crowding in the structure of **6**. The Sb–S–C angles are within the expected range of 95–100°.

Experimental

All experiments were carried out under nitrogen using standard vacuum-line techniques. Solvents were distilled under nitrogen from sodium-benzophenone [diethyl ether, tetrahydrofuran, light petroleum (b.p. 40–60 °C)], sodium (toluene) or calcium hydride (acetonitrile, dichloromethane). The NMR solvents were stored over 4 Å molecular sieves under nitrogen or argon and degassed by several freeze–thaw cycles. The compounds $2,4,6\text{-}Me_3C_6H_2SH$ (R^1SH),[9] $2,4,6\text{-}Pr^i{}_3C_6H_2SH$ (R^2SH),[9] $2,4,6\text{-}Bu^t{}_3C_6H_2SH$ (R^3SH),[10] $2,4,6\text{-}Me_3C_6H_2SeH$ (R^1SeH),[2b] $2,4,6\text{-}Pr^i{}_3C_6H_2SeH$ (R^2SeH),[2b] $2,4,6\text{-}Bu^t{}_3C_6H_2SeH$ (R^3SeH),[2a] and $2,4,6\text{-}Me_3C_6H_2TeH$ (R^1TeH)[2d] were prepared as described. Melting points are uncorrected. The NMR spectra were recorded using JEOL EX90Q and EX270 instruments. The bismuth and antimony complexes described were prepared either by protolysis of bismuth and antimony amides (method A) or from $BiCl_3$ and $SbCl_3$ by halide exchange (method B). One representative example for each method is given below.

$Bi[N(SiMe_3)_2]_3$.—Bismuth and antimony bis(trimethylsilyl)-amides have been mentioned before, without experimental detail.[11] The solid $Na[N(SiMe_3)_2]$ (16.9 g, 92.3 mmol) in thf (60 cm^3) was added to $BiCl_3$ (9.7 g, 30.8 mmol) in thf (40 cm^3) at room temperature. The mixture was stirred for 3 h. After removal of the solvent *in vacuo* the residue was extracted with light petroleum (3 × 50 cm^3), filtered and concentrated. The product was obtained as a yellow crystalline solid on cooling to −16 °C (9.0 g, 42.5%). NMR (C_6D_6): ^1H, δ 0.37; ^{13}C, δ 6.60.

The compound $Sb[N(SiMe_3)_2]_3$[11] was prepared similarly as white crystals (54.5%). NMR (C_6D_6): ^1H, δ 0.42; ^{13}C, δ 6.76.

$Bi(SR^1)_3$ **1** (*Method A*).—The compound $Bi[N(SiMe_3)_2]_3$ (0.98 g, 1.42 mmol) in light petroleum (10 cm^3) was added to R^1SH (1.0 g, 4.25 mmol) in light petroleum (40 cm^3) at room temperature. The red solution formed was stirred for 1 h. The solvent was removed *in vacuo* and the residue recrystallised from acetonitrile–ethyl acetate (3:1 v/v) to give orange crystals of **1** (1.1 g, 1.2 mmol, 86%).

Compounds **2**, **3**, **5** and **7**–**12** were prepared similarly. The formation of a dark precipitate was sometimes observed when the amide was added at room temperature. This can be prevented by lowering the temperature during the addition step.

$Sb(SeR^1)_3$ **4** (*Method B*).—A 1.0 mol dm^{-3} solution (13.0 cm^3) of $Li[BHEt_3]$ (13.0 mmol) in thf was added to $R^1{}_2Se_2$ (2.6 g, 6.5 mmol) in thf (40 cm^3) at room temperature and the solution formed was stirred for 30 min before being cooled to −78 °C. To this was added dropwise a solution of $SbCl_3$ (1.0 g, 4.4 mmol) in thf (10 cm^3) at −78 °C and the mixture was warmed to room temperature and stirred for 2 h. It was pumped to dryness and the residue extracted with toluene. The product was filtered off and recrystallised from acetonitrile–ethyl acetate (3:1) to give **4** as a yellow microcrystalline solid (1.6 g, 51%). Compounds **2** and **6** were prepared similarly.

Bulk Decomposition Studies.—Typically, about 100 mg of the compound were placed in the bottom of a Schlenk tube connected to a high vacuum line. The tube was then evacuated to 10^{-6} mbar before its tap was closed. The bottom two-thirds of the Schlenk tube were then inserted into a tube furnace. The decomposition temperatures are given in Table 3. The organic by-products condensed in the cooler part of the Schlenk tube and were analysed by mass spectrometry.

X-Ray Crystallography.—X-Ray measurements on $Sb(SR^2)_3$ **6** and $Bi(SeR^2)_3$ **7** were carried out using an Enraf-Nonius FAST TV area detector diffractometer and graphite-monochromated Mo-Kα radiation [λ(Mo-Kα) = 0.710 69 Å]. The crystals of **7** were of poor quality, and the structure could not be refined below 9%. Therefore only the structure of **6** is reported in detail. It was solved by the Patterson method using SHELXS[12] and refined by full-matrix least-squares techniques using SHELX 80.[13] A DIFABS[14] correction was made at the isotropic refinement stage. Hydrogen atoms were allowed to ride on their parent carbons (r_{CH} = 0.96 Å) in calculated positions, a common U_{iso} being refined for all. Atomic positional parameters are listed in Table 5.

Crystal data. $C_{45}H_{69}S_3Sb$, M_r = 827.93 monoclinic, space group *Cc*, $a = 22.969(8)$, $b = 22.848(8)$, $c = 9.250(5)$ Å, $\beta = 105.40(2)°$, $U = 4680(3)$ Å^3, $Z = 4$, $D_c = 1.175$ g cm^{-3}, $F(000) = 1752$; crystal dimensions 0.55 × 0.30 × 0.28 mm.

Data collection and refinement. $2.40 \leqslant \theta \leqslant 29.84°$; $-15 \leqslant h \leqslant 30$, $-29 \leqslant k \leqslant 30$, $-12 \leqslant l \leqslant 8$; $\mu = 0.750$ mm^{-1}. 15 345 Reflections collected of which 6911 were independent ($R_{int} = 0.0722$). The data:restraints:parameter ratio was 6908:2:461. Goodness of fit on F^2 was 0.614, final *R* indices [$I > 2\sigma(I)$] were $R^1 = 0.0386$, $wR^2 = 0.0755$; (all data) $R^1 = 0.1028$, $wR^2 = 0.1017$. Weighting scheme used $w =$

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* Preliminary bond lengths and angles for compound **7**: Bi–Se(1) 2.659(8), Bi–Se(2) 2.630(8) and Bi–Se(3) 2.711(8) Å; Se(1)–Bi–Se(2) 103.3(2), Se(1)–Bi–Se(3) 92.3(2) and Se(2)–Bi–Se(3) 100.0(3)°. Space group $P\bar{1}$, $a = 14.516(3)$, $b = 16.755(9)$, $c = 22.338(8)$ Å, $\alpha = 95.98(1)$, $\beta = 103.69(1)$ and $\gamma = 109.75(1)°$.

Table 5 Atomic coordinates (× 10⁴) for compound **6**

Atom	*x*	*y*	*z*
Sb	−442(1)	−2 846(1)	−8 063(1)
S(1)	−414(1)	−3 646(1)	−9 786(2)
C(1)	−1 194(3)	−3 701(3)	−10 764(8)
C(2)	−1 614(5)	−3 969(4)	−10 136(10)
C(3)	−2 176(4)	−4 054(4)	−10 996(10)
C(4)	−2 395(4)	−3 873(3)	−12 502(9)
C(5)	−1 972(4)	−3 571(4)	−13 038(10)
C(6)	−1 383(4)	−3 471(3)	−12 271(8)
C(7)	−945(4)	−3 168(3)	−12 985(8)
C(8)	−1 225(5)	−2 700(4)	−14 066(9)
C(9)	−623(4)	−3 612(4)	−13 748(7)
C(10)	−1 423(4)	−4 231(4)	−8 555(8)
C(11)	−1 906(5)	−4 146(4)	−7 717(8)
C(12)	−1 260(5)	−4 876(3)	−8 592(8)
C(13)	−3 025(4)	−3 980(5)	−13 382(10)
C(14)	−3 086(5)	−4 373(5)	−14 608(15)
C(15)	−3 388(5)	−3 464(5)	−13 799(12)
S(2)	−682(1)	−2 105(1)	−9 996(2)
C(16)	−1 004(4)	−1 603(4)	−8 897(7)
C(17)	−1 566(4)	−1 696(4)	−8 689(8)
C(18)	−1 774(4)	−1 312(4)	−7 791(9)
C(19)	−1 441(4)	−836(4)	−7 134(9)
C(20)	−904(5)	−732(5)	−7 454(12)
C(21)	−658(4)	−1 098(4)	−8 334(9)
C(22)	−61(5)	−940(5)	−8 654(10)
C(23)	325(5)	−503(4)	−7 642(13)
C(24)	−164(5)	−744(4)	−10 251(11)
C(25)	−1 666(5)	−422(5)	−6 097(12)
C(26)	−1 494(5)	−714(5)	−4 539(12)
C(27)	−2 253(6)	−227(5)	−6 536(13)
C(28)	−1 956(4)	−2 192(4)	−9 398(9)
C(29)	−2 333(6)	−2 069(5)	−11 009(11)
C(30)	−2 405(5)	−2 414(5)	−8 615(12)
S(3)	641(1)	−2 708(1)	−7 279(2)
C(31)	783(3)	−2 918(3)	−5 339(6)
C(32)	793(4)	−2 483(4)	−4 257(8)
C(33)	945(4)	−2 661(4)	−2 753(9)
C(34)	1 079(4)	−3 229(4)	−2 312(8)
C(35)	1 065(4)	−3 656(5)	−3 388(9)
C(36)	904(3)	−3 507(3)	−4 928(8)
C(37)	854(5)	−4 012(4)	−6 054(10)
C(38)	383(5)	−4 413(4)	−5 970(9)
C(39)	1 471(4)	−4 312(4)	−5 811(10)
C(40)	1 263(5)	−3 368(5)	−650(9)
C(41)	1 920(6)	−3 211(5)	−2(9)
C(42)	1 133(6)	−3 979(5)	−291(9)
C(43)	660(4)	−1 847(4)	−4 617(9)
C(44)	1 228(5)	−1 504(5)	−4 228(14)
C(45)	181(6)	−1 597(5)	−3 922(14)

$[\sigma^2(F_o)^2 + (0.029P)^2]^{-1}$, where $P = \frac{1}{3}[\max. (F_o^2, 0) + 2 F_c^2]$. The largest difference peak and hole were 0.891 and −0.338 e Å^{-3}, respectively. The structure is a racemic twin, with the occupancies of primary and secondary components being 0.54 and 0.46.

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

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