

Toluene-3,4-dithiol (H_2tdt) Complexes of Group 5B Halides. Observations of Lone-pair Stereochemical Activity and Redox Behaviour. Crystal and Molecular Structures of $[AsCl(tdt)]$ and $[PPh_4][Sb(tdt)_3]$ *

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Reactions of toluene-3,4-dithiol (H_2tdt) with the Group 5B chlorides MCl_3 ($M = As, Sb, \text{ or } Bi$) have been investigated under conditions of varying stoichiometry. Complexes of the types $[MCl(tdt)]$ ($M = As, Sb, \text{ or } Bi$), $[Sb(Htdt)(tdt)]$, $[NEt_3H][Bi(tdt)_2]$, and $[Y][Sb(tdt)_3]$ ($Y = NEt_4$ or PPh_4) have been isolated and characterised by spectroscopic (i.r. and 1H n.m.r.) data. For the $[MCl(tdt)]$ series, obtained following 1 : 1 addition, ligand (SH) protons are removed as HCl and a tetrahedral geometry with full stereochemical participation of the lone pair of electrons associated with M^{III} is confirmed for $M = As$ by an X-ray crystal structure determination. The complexes $[Sb(Htdt)(tdt)]$ and $[NEt_3H][Bi(tdt)_2]$, resulting from 1 : 2 addition, are quite dissimilar with only the latter experiencing full replacement of ligand (SH) protons. For $[Sb(Htdt)(tdt)]$ there is strong evidence to suggest that one of the ligand (SH) protons remains intact giving rise to a neutral species based on Sb^{III} . Attempts to remove this proton to give the anion $[Sb(tdt)_2]^-$ have been unsuccessful. For the $[Y][Sb(tdt)_3]$ complexes, obtained following 1 : 3 addition, all ligand (SH) protons are removed and an X-ray crystal structure determination for $Y = PPh_4$ shows the anion as a slightly distorted octahedron following aerial oxidation $Sb^{III} \rightarrow Sb^V$. Crystals of $[AsCl(tdt)]$ (1) are monoclinic, space group $P2_1/c$, $Z = 4$, $a = 6.127(5)$, $b = 15.773(11)$, $c = 9.768(8)$ Å, and $\beta = 91.0(1)^\circ$. Crystals of $[PPh_4][Sb(tdt)_3]$ (2) are monoclinic, space group $P2_1$, $Z = 2$, $a = 10.464(7)$, $b = 12.825(9)$, $c = 16.433(8)$ Å, and $\beta = 102.5(1)^\circ$. 113,884 Reflections above background have been collected on a diffractometer and the structures refined to R 0.052, 0.120 respectively. In (1) the arsenic atom is three-co-ordinate [$As-Cl$ 2.236(3); $As-S$ 2.226(3), 2.209(3) Å]. In $[Sb(tdt)_3]^-$, the antimony atom is six-co-ordinate in a distorted octahedral environment with $Sb-S$ in the range 2.34(3)—2.50(2) Å.

Toluene-3,4-dithiol (H_2tdt) is an attractive choice as a potential S,S' -bidentate metal scavenger. Complexes with a variety of transition and post-transition metal halide (X) acceptors have been noted, the majority of these following incipient proton (SH) loss and expulsion as HX .¹

Specifically for Group 5B elements, Hunter² has reported the neutral complexes $[Sb_2(tdt)_3]$ and $[Bi_2(tdt)_3]$. The polymeric Bi^{III} complex $\{[BiCl(tdt)]_n\}$ is known and appears to give 1 : 2 adducts with pyridine, 2,2'-bipyridyl, and 1,10-phenanthroline.³ The preparation and redox behaviour of a series of complexes including $[Sb_2(tdt)_3]$, $[Bi_4(tdt)_6]$, $[Y][M(tdt)_2]$ ($Y = NEt_4$, PPh_4 , $AsPh_4$, $SbPh_4$, or NBu_4^+ ; $M = As^{III}$, Sb^{III} , or Bi^{III}), and $[Y][M(tdt)_3]$ ($Y = NEt_4$ or $AsPh_4$, $M = Sb^V$) have been described recently but precise characterisation is lacking.⁴ A previous study by one of us (S. O. W.)⁵ of the 1 : 1 and 1 : 2 complexes with Sb^{III} was initiated as part of a programme concerned with the chemotherapeutic treatment of bilharzia. Several aspects emerging from this and other previous work are re-evaluated here. What is of especial interest in these complexes, and indeed for M^{III} S-bonded systems ($M = \text{Group 5B element}$)

in general, is the stereochemical influence of the lone pair of electrons associated with M^{III} in terms of structure and chemical reactivity.

Experimental

All chemicals were of reagent grade and were used without further purification. Solvents were stored over either CaH_2 or P_2O_5 and distilled under a nitrogen atmosphere prior to use. Because of the air and/or moisture sensitivity of many of the reactants and products, manipulations and synthetic work on these systems required the use either of vacuum-line techniques or of a N_2 -filled gloved box, or both. I.r. spectra were recorded on a Perkin-Elmer 580B spectrophotometer with samples between CsI plates as Nujol mulls or in solution. 1H N.m.r. spectra were recorded on a Perkin-Elmer R34 instrument (220 MHz) for $CDCl_3$ solutions doped with tetramethylsilane as internal reference. Elemental analyses were carried out by Butterworth Laboratories Ltd., Teddington, Middlesex. Chloride was determined by the Volhard titration.

Preparation of the Complexes.—Chloro[*toluene-2,3-dithiolato*(2-)]arsenic(III), (1). Arsenic trichloride (0.54 cm³, 6.4 mmol) was added to a solution of toluene-3,4-dithiol (1.0 g, 6.9 mmol) in chloroform (50 cm³). The resulting mixture was heated under reflux for 20 min when a yellow solution was obtained. Chloroform was slowly removed *in vacuo* leaving the

* Chloro[*toluene-3,4-dithiolato*(2-)- S,S']arsenic(III) and tetraphenylphosphonium tris[*toluene-3,4-dithiolato*(2-)- S,S']antimonate(V) respectively.

Supplementary data available (No. SUP 56071, 8 pp.): thermal parameters, H-atom co-ordinates, remaining dimensions. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xviii–xix. Structure factors are available from the editorial office.

product as a yellow solid. Recrystallisation from methanol gave long yellow needles (yield 1.5 g, 85%) (Found: C, 31.7; H, 2.2; Cl, 13.4. $C_7H_6AsClS_2$ requires C, 31.8; H, 2.3; Cl, 13.4%). I.r. (ν_{max}): 1 252, 1 112, 1 035, 871, 866, 804, 683, 631, 537, 482, 441, 427, 398, 304, and 251 cm^{-1} (Nujol). N.m.r.: δ_H 2.35 (3 H, s, CH_3); 7.05 and 7.41–7.48 (3 H, m, aromatic C_6H_3).

Chloro[toluene-3,4-dithiolato(2-)]antimony(III). Toluene-3,4-dithiol (1.05 g, 6.7 mmol) was added to a hot solution of $SbCl_3$ (1.53 g, 6.7 mmol) in chloroform (50 cm^3) to give a deep yellow solution. This was cooled in ice when a yellow solid precipitated out. The *product* was recrystallised from a methanol solution doped with dimethyl sulphoxide (dmsO) to give fine yellow needles (yield 0.6 g, 25%), m.p. 141–142 °C (Found: C, 27.0; H, 1.9; Cl, 11.6; S, 20.9. $C_7H_6ClS_2Sb$ requires C, 27.0; H, 1.9; Cl, 11.4; S, 20.6%). I.r. (ν_{max}): 1 245, 1 108, 810, 679, 628, 538, 475, 431, 371, 334, and 282 cm^{-1} (Nujol). N.m.r.: δ_H 2.33 (3 H, s, CH_3); 6.93 and 7.38–7.46 (3 H, m, aromatic C_6H_3).

Chloro[toluene-3,4-dithiolato(2-)]bismuth(III). Chloroform (50 cm^3) was distilled onto a mixture of $BiCl_3$ (2.0 g, 6.4 mmol) and toluene-3,4-dithiol (1.03 g, 6.5 mmol) and the whole heated at reflux for 2 h under an atmosphere of dry nitrogen. The resulting brown suspension was allowed to settle and the colourless solution was decanted off. The remaining brown solid was collected and pumped dry. Recrystallisation of the *product* from methanol–dmsO gave very dark brown needles, m.p. 252–254 °C (decomp.) (Found: C, 21.7; H, 1.7; S, 16.2. $C_7H_6BiClS_2$ requires C, 21.1; H, 1.5; S, 16.1%). I.r. (ν_{max}): 1 252, 1 143, 1 106, 866, 799, 680, 533, 431, 373, and 328 cm^{-1} (Nujol). N.m.r.: δ_H 2.28 (3 H, s, CH_3); 6.87 and 7.36 (3 H, m, aromatic C_6H_3).

[Toluene-3,4-dithiolato(2-)][toluene-3,4-dithiolato(1-)]antimony(III). Toluene-3,4-dithiol (2.4 g, 15 mmol) was added to a hot solution of $SbCl_3$ (1.6 g, 7 mmol) in methanol (50 cm^3). A deep yellow solution immediately formed. This solution was allowed to cool slowly to give the *product* as a microcrystalline yellow solid. Recrystallisation from methanol gave chunky yellow crystals (yield 10.1 g, 30%) (Found: C, 39.7; H, 2.8; S, 30.2. $C_{14}H_{13}S_4Sb$ requires C, 39.0; H, 3.0; S, 29.7%). I.r. (ν_{max}): 3 040, 2 860, 2 335, 1 584, 1 458, 1 379, 1 256, 1 112, 1 031, 863, 807, 680, 631, 540, 438, 365, 331, and 290 cm^{-1} ($CHCl_3$ solution). N.m.r.: δ_H 2.28 (6 H, s, CH_3), 3.49 (1 H, s, SH); 6.87 and 7.25–7.35 (6 H, m, aromatic C_6H_3).

Triethylammonium bis[toluene-3,4-dithiolato(2-)]bismuthate(III). Bismuth trichloride (0.92 g, 2.9 mmol) was added to a solution of toluene-3,4-dithiol (0.92 g, 5.8 mmol) and triethylamine (1.63 cm^3 , 11.7 mmol) in methanol (50 cm^3). The mixture was gently heated at reflux with magnetic stirring under an atmosphere of dry nitrogen for 30 min. On cooling, the *product* separated as a brown solid which was filtered off and collected. After several washings with water, recrystallisation from acetone provided deep brown platelets (Found: C, 39.3; H, 4.6; N, 2.6; S, 20.1. $C_{20}H_{28}BiNS_4$ requires C, 38.7; H, 4.5; N, 2.3; S, 20.7%). I.r. (ν_{max}): 1 581, 1 246, 1 104, 1 030, 863, 807, 681, 631, 542, 470, 437, 304, and 271 cm^{-1} (Nujol). N.m.r.: δ_H 1.25 (9 H, t, CH_3-CH_2-), 2.20 [6 H, s, CH_3 (aromatic ring)], 3.05 (6 H, q, CH_3-CH_2-); 7.02 and 7.48 (6 H, m, aromatic C_6H_3).

Tetraethylammonium tris[toluene-3,4-dithiolato(2-)]antimonate(V). A solution of antimony trichloride (0.69 g, 3 mmol) in methanol (20 cm^3) was added to a solution containing toluene-3,4-dithiol (0.95 g, 6 mmol), triethylamine (1.7 cm^3 , 12 mmol) and tetraethylammonium chloride (0.56 g, 3 mmol) dissolved in methanol (40 cm^3). A vigorous reaction ensued to give a deep red solution. On standing overnight a dark purple-red solid separated from the solution. This was collected and washed with warm water (3 \times 25 cm^3) until the washings gave a negative test for chloride. The purple-violet *product* was further washed with boiling water (2 \times 25 cm^3) and diethyl ether (3 \times 25 cm^3) and finally recrystallised from chloroform–

methanol (1:10) as almost black crystals, m.p. 149–150 °C (Found: C, 47.5; H, 5.4; N, 2.5; S, 27.0. $C_{29}H_{38}NS_6Sb$ requires C, 48.7; H, 5.3; N, 2.0; S, 26.9%). I.r. (ν_{max}): 3 041, 2 860, 1 585, 1 449, 1 390, 1 367, 1 250, 1 169, 1 105, 1 037, 999, 869, 807, 681, 636, 546, 476, 437, 351, and 317 cm^{-1} (CH_2Cl_2 solution). N.m.r.: δ_H 1.07 (12 H, t, CH_3-CH_2-), 2.22 [9 H, s, CH_3 (aromatic ring)], 2.93 (8 H, q, CH_3-CH_2-); 6.71 and 7.25 (9 H, m, aromatic C_6H_3).

Tetraphenylphosphonium tris[toluene-3,4-dithiolato(2-)]antimonate(V), (2). Antimony trichloride (0.44 g, 1.9 mmol) was added to a solution containing toluene-3,4-dithiol (0.59 g, 3.8 mmol) and triethylamine (1.1 cm^3 , 7.6 mmol) in methanol (40 cm^3). The resulting red solution was heated at reflux for 20 min. Addition of tetraphenylphosphonium bromide (0.80 g, 1.9 mmol) to this solution resulted in immediate precipitation of the *product* as a purple solid. Recrystallisation from chloroform–methanol (1:10) provided very dark purple platelets, m.p. 192–193 °C (Found: C, 58.5; H, 3.8. $C_{45}H_{38}PS_6Sb$ requires C, 58.5; H, 4.1%). I.r. (ν_{max}): 1 587, 1 260, 1 108, 1 042, 1 000, 874, 803, 691, 637, 540, 480, 442, 355, and 321 cm^{-1} (Nujol). N.m.r.: δ_H 2.13 [9 H, s, CH_3 (aromatic ring)]; 6.58 and 7.11 (9 H, m, aromatic C_6H_3); 7.5–7.8 (20 H, m, C_6H_5).

A repeat of this reaction using antimony potassium tartrate (0.62 g, 1.9 mmol) in place of antimony trichloride and following similar work-up procedures provides an alternative route to this purple-violet product.

Structure Determinations.—Suitable crystals of (1) and (2) were selected from recrystallised samples obtained as described above and placed in Lindemann tubes. Precession photographs established preliminary cell constants and space groups. Crystals of (1) were of good quality but those of (2) were execrable. Crystals of (2) were all twinned and in the diffraction pattern peaks were broad and weak. However we chose the best crystal of (2) we could find. Crystals of both compounds were transferred to a Stoe Stadi-2 diffractometer and data were taken *via* ω scans of width $(1.5 + 0.5 \sin \mu / \tan \theta)$. The scan speed was 0.033° s⁻¹ and the background was measured at the ends of the ω scan for 20 s. Measurements of standard reflections showed no deterioration. Details of cell constants, data collection, and refinement details are given in Table 1. An absorption correction was applied to (1), using SHELX 76,⁶ transmission factors being between 0.67 and 0.20.

In both structures, the Patterson function was used to determine the positions of the heaviest atoms. In (1) the remaining atoms were located from Fourier maps. Hydrogen atoms were included in calculated positions and their thermal parameters refined. Hydrogen atoms on the same carbon atom were given an equivalent thermal parameter. Non-hydrogen atoms were refined anisotropically *via* full-matrix least squares and the final *R* was 0.052 (*R'* 0.054).

The structure of (2) was more difficult to solve because of the heavy atom on a pseudo-mirror plane and the poor quality data. The seven unique phenyl rings were all refined as rigid groups, each with a common thermal parameter. The methyl group on one of the tdt anions was disordered and was refined in two possible positions with population parameters of *x* and 1 – *x* respectively. Hydrogen atoms were not included. Antimony, phosphorus, and sulphur were refined anisotropically and carbon isotropically *via* full-matrix least squares to *R* 0.12 (*R'* 0.12).

Scattering factors and dispersion corrections were taken from ref. 7. The final difference-Fourier maps showed no important features and in the final cycles of refinement no shift was greater than 0.1 σ . Calculations were carried out using SHELX 76⁶ at the University of Manchester Computer Centre. Final coordinates are given in Tables 2 and 3, bond lengths and angles in Table 4.

Table 1. Crystal data and refinement details for [AsCl(tdt)] (1) and [PPh₄][Sb(tdt)₃] (2)

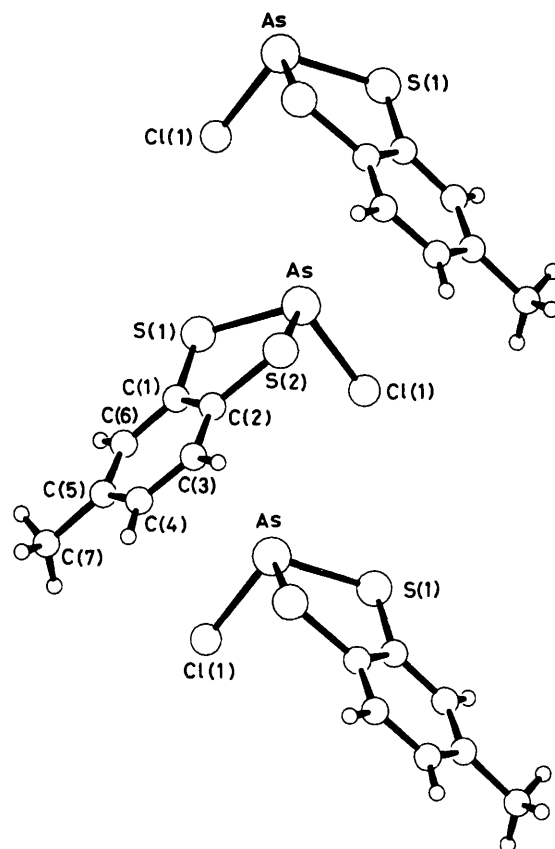
Compound	(1)	(2)
Formula	C ₇ H ₆ AsClS ₂	C ₄₅ H ₃₈ PS ₆ Sb
<i>M</i>	254.5	923.4
Crystal class	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁
Absences	0 <i>k</i> 0; <i>k</i> = 2 <i>n</i> + 1 <i>h</i> 0 <i>l</i> ; <i>l</i> = 2 <i>n</i> + 1	0 <i>k</i> 0; <i>k</i> = 2 <i>n</i> + 1
<i>a</i> /Å	6.127(5)	10.464(7)
<i>b</i> /Å	15.773(11)	12.825(9)
<i>c</i> /Å	9.768(8)	16.433(8)
β/°	91.0(1)	102.5(1)
<i>U</i> /Å ³	943.85	2 152.9
<i>F</i> (000)	520	940
<i>Z</i>	4	2
<i>D</i> _m /g cm ⁻³	1.84	1.43
<i>D</i> _c /g cm ⁻³	1.86	1.42
μ/cm ⁻¹	44.3	9.97
λ/Å	0.7107	0.7107
Crystal size (mm)	1.25 × 0.10 × 0.40	1.6 × 0.6 × 0.05
Rotation axis	<i>a</i>	<i>b</i>
2θ max./°	50	40
No. of data measured	1 480	2 290
No. of data used in refinement	1 113	884
Criterion for data inclusion	<i>I</i> > 3σ(<i>I</i>)	<i>I</i> > 3σ(<i>I</i>)
Final <i>R</i> value	0.052	0.120

Table 2. Atomic co-ordinates (× 10⁴) for [AsCl(tdt)] (1) with estimated standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
As(1)	2 363(2)	2 348(1)	3 415(1)
S(2)	— 892(4)	2 584(1)	4 320(3)
S(1)	3 587(4)	3 614(1)	4 018(2)
Cl(1)	3 859(4)	1 554(2)	5 080(3)
C(1)	1 685(13)	3 874(5)	5 305(8)
C(2)	— 251(13)	3 430(5)	5 441(8)
C(3)	— 1 715(14)	3 653(6)	6 442(8)
C(4)	— 1 205(13)	4 313(6)	7 344(8)
C(5)	716(15)	4 753(5)	7 226(8)
C(6)	2 199(14)	4 519(5)	6 226(8)
C(7)	1 328(23)	5 455(7)	8 222(11)

Results and Discussion

1:1 Addition.—Equimolar addition of chloroform solutions of MCl₃ and toluene-3,4-dithiol (H₂tdt) provides the complexes [MCl(tdt)] (M = As, Sb, or Bi) following HCl expulsion. All are crystalline solids, tolerably soluble in polar organic solvents, but decompose on prolonged exposure to air. Proton (SH) loss is confirmed by the absence of the ligand δ_{SH} 3.56 and 3.74 signals in the ¹H n.m.r. spectra and the complete removal of the sharp ν(S—H) stretching vibration located at 2 548 cm⁻¹ in the free ligand. The ¹H n.m.r. spectra show a sharp singlet for the methyl group in the region δ 2.28–2.35 and a multiplet at δ 6.87–7.48 for the aromatic protons consistent with complex formation. In the far-i.r. region (400–200 cm⁻¹), the spectral pattern shows one prominent metal–chlorine stretching band, e.g., ν(As–Cl) 304 and ν(Sb–Cl) 282 cm⁻¹, along with several minor bands associated with ν(M–Cl), ν(M–S), and internal ligand mode coupling.⁸ Our preference for a four electron-pair AX₂YE formulation, as found for the related Sb^{III} dithiolato-complex 2-chloro-2-stiba-1,3-dithiacyclopentane⁹ which has a three-co-ordinate SbS₂Cl arrangement with a stereochemically

**Figure 1.** The packing of the AsCl(tdt) molecules of (1) along the *b* axis, showing the As...C interactions [3.32(1)–3.63(1) Å]

active lone pair of electrons occupying the remaining tetrahedral site, is confirmed in the case of [AsCl(tdt)] (1) by an X-ray crystal structure determination. The Sb^{III} analogue is presumed to have a similar structure, whilst the identity of our Bi^{III} complex, which has been reported previously as a polymeric material,³ is under current scrutiny.

Crystal Structure of [AsCl(tdt)] (1).—The unit cell of (1) contains units of AsCl(tdt) which are packed together along the *b* direction via weak As...Ph contacts (Figure 1). In each individual molecule the arsenic atom is three-co-ordinate, being bonded to a tdt ligand via two sulphur atoms [As–S 2.226(3), 2.209(3) Å] and to a chlorine atom [As–Cl 2.236(3) Å]. The three angles subtended at the arsenic atom are S(2)–As–S(1) 92.62(9), S(1)–As–Cl(1) 100.34(10), and S(2)–As–Cl(1) 99.43(10)°. The arsenic co-ordination sphere can therefore be categorised as tetrahedral, with the lone pair occupying one site. The angles subtended at arsenic are all much less than the regular tetrahedral angle of 109.47°, thus showing the dominant space-filling requirement of the lone pair.

A search of the Cambridge Data Centre files has revealed five similar AX₂YE systems for As^{III} in which the full stereochemical commitment of the lone pair is demonstrated. Three of these contain AsS₃ cores but the other two, namely, 5-chloro-1,4,6,5-oxadithiarsocane¹⁰ and 2-chloro-1,3,6,2-trithiarsocane¹¹ contain AsClS₂ cores similar to that found in (1). In these two structures bond lengths are As–S 2.259, 2.247; As–Cl 2.356 and As–S 2.268, 2.248; As–Cl 2.268 Å respectively. In (1) the five-membered AsS₂C₂ ring units possess As–S bond lengths significantly shorter at 2.226 and 2.209 Å, presumably as

Table 3. Atomic co-ordinates ($\times 10^4$) for $[\text{PPh}_4][\text{Sb}(\text{tdt})_3]$ (2) with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Sb(1)	728(7)	2 500(0)	2 801(4)	C(96)	1 051(112)	104(56)	776(53)
S(1)	3 002(25)	3 036(22)	3 399(20)	C(97)	−244(181)	−2 489(66)	1 177(76)
S(2)	391(25)	2 879(18)	4 134(19)	Cation carbon atoms			
S(3)	−1 601(33)	2 225(16)	2 212(22)	C(11)	6 322(74)	1 291(57)	8 331(45)
S(4)	294(26)	4 289(16)	2 201(21)	C(12)	6 680(74)	1 799(57)	9 097(45)
S(5)	1 517(39)	1 883(21)	1 599(21)	C(13)	7 290(74)	1 244(57)	9 805(45)
S(6)	937(35)	666(18)	3 223(18)	C(14)	7 542(74)	182(57)	9 747(45)
P(1)	5 588(24)	2 022(16)	7 403(16)	C(15)	7 184(74)	−326(57)	8 981(45)
C(61)	3 052(105)	3 721(64)	4 352(56)	C(16)	6 574(74)	228(57)	8 272(45)
C(62)	3 952(73)	4 502(65)	4 678(53)	C(21)	4 136(55)	1 368(43)	6 833(45)
C(63)	3 760(71)	5 045(67)	5 395(52)	C(22)	3 380(55)	688(43)	7 195(45)
C(64)	2 533(69)	5 067(49)	5 582(45)	C(23)	2 314(55)	176(43)	6 699(45)
C(65)	1 573(77)	4 345(75)	5 207(60)	C(24)	2 004(55)	345(43)	5 840(45)
C(66)	1 795(81)	3 716(59)	4 549(52)	C(25)	2 760(55)	1 025(43)	5 478(45)
C(67a)	2 392(126)	5 567(112)	6 326(74)	C(26)	3 826(55)	1 537(43)	5 974(45)
C(67b)	4 791(101)	5 647(134)	5 859(93)	C(31)	4 965(80)	3 215(39)	7 670(43)
C(71)	−1 378(73)	4 313(56)	1 684(62)	C(32)	3 650(80)	3 379(39)	7 679(43)
C(72)	−1 787(71)	5 237(54)	1 224(60)	C(33)	3 242(80)	4 348(39)	7 915(43)
C(73)	−3 110(77)	5 259(52)	756(61)	C(34)	4 148(80)	5 151(39)	8 140(43)
C(74)	−3 848(73)	4 358(56)	630(55)	C(35)	5 462(80)	4 987(39)	8 130(43)
C(75)	−3 447(81)	3 454(54)	1 116(64)	C(36)	5 871(80)	4 018(39)	7 895(43)
C(76)	−2 140(78)	3 419(47)	1 589(54)	C(41)	6 633(66)	2 284(53)	6 834(43)
C(77)	−3 491(116)	6 156(74)	259(86)	C(42)	7 626(66)	1 550(53)	6 865(43)
C(91)	1 176(108)	526(55)	1 578(56)	C(43)	8 543(66)	2 539(53)	5 844(43)
C(92)	691(114)	70(59)	2 242(51)	C(44)	8 467(66)	2 539(53)	5 844(43)
C(93)	212(109)	−980(54)	2 091(48)	C(45)	7 474(66)	3 274(53)	5 813(43)
C(94)	176(108)	−1 427(49)	1 305(51)	C(46)	6 557(66)	3 146(53)	6 308(43)
C(95)	569(106)	−930(55)	655(45)				

Table 4. Selected bond distances (Å) and angles (°) in complexes (1) and (2)

(a) Complex (1)		(b) Complex (2)	
As(1)–S(1)	2.209(3)	Sb(1)–S(1)	2.468(29)
As(1)–S(2)	2.226(3)	Sb(1)–S(2)	2.343(35)
As(1)–Cl(1)	2.236(3)	Sb(1)–S(3)	2.444(35)
S(2)–C(2)	1.767(8)	Sb(1)–S(4)	2.499(24)
S(1)–C(1)	1.777(8)	Sb(1)–S(5)	2.432(30)
C(1)–C(2)	1.368(11)	Sb(1)–S(6)	2.448(24)
C(1)–C(6)	1.390(12)	S(1)–C(61)	1.79(7)
C(2)–C(3)	1.384(11)	S(2)–C(66)	1.83(6)
C(3)–C(4)	1.397(13)	S(3)–C(76)	1.86(6)
C(4)–C(5)	1.373(13)	S(4)–C(71)	1.77(7)
C(5)–C(6)	1.396(12)	S(5)–C(91)	1.78(7)
C(5)–C(7)	1.516(13)	S(6)–C(92)	1.75(7)
S(2)–As(1)–S(1)	92.62(9)	S(1)–Sb(1)–S(2)	84.1(9)
S(2)–As(1)–Cl(1)	99.43(10)	S(1)–Sb(1)–S(3)	172.1(8)
S(1)–As(1)–Cl(1)	100.34(10)	S(2)–Sb(1)–S(3)	93.5(10)
As(1)–S(2)–C(2)	100.45(29)	S(1)–Sb(1)–S(4)	88.8(8)
As(1)–S(1)–C(1)	99.97(28)	S(2)–Sb(1)–S(4)	97.3(9)
S(1)–C(1)–C(2)	121.6(6)	S(3)–Sb(1)–S(4)	84.0(8)
S(1)–C(1)–C(6)	118.8(6)	S(1)–Sb(1)–S(5)	86.9(11)
C(2)–C(1)–C(6)	119.5(7)	S(2)–Sb(1)–S(5)	166.6(12)
S(2)–C(2)–C(1)	120.2(6)	S(3)–Sb(1)–S(5)	96.7(12)
S(2)–C(2)–C(3)	119.4(6)	S(4)–Sb(1)–S(5)	92.5(10)
C(1)–C(2)–C(3)	120.4(7)	S(1)–Sb(1)–S(6)	97.8(10)
C(2)–C(3)–C(4)	119.7(8)	S(2)–Sb(1)–S(6)	87.5(8)
C(3)–C(4)–C(5)	120.4(8)	S(3)–Sb(1)–S(6)	89.6(10)
C(4)–C(5)–C(6)	119.6(7)	S(4)–Sb(1)–S(6)	172.3(11)
C(4)–C(5)–C(7)	121.2(8)	S(5)–Sb(1)–S(6)	83.8(10)
C(6)–C(5)–C(7)	119.0(8)		
C(1)–C(6)–C(5)	120.2(8)		

a result of π delocalisation incorporating the aromatic ring. The S–C (1.77 Å) and As–Cl bond lengths (2.236 Å) are also marginally shorter than the corresponding bond distances in the two AsClS_2 counterparts.

Retention of sp^2 hybridisation within the aromatic ring is

confirmed by carbon bond angles close to 120° . The angle between the AsS_2 and S_2C_6 planes is 22.3° . The As atom is 0.58 Å from the S_2C_6 plane.

The molecules pack together forming a polymeric chain along b (see Figure 1). There are no $\text{As} \cdots \text{Cl}_3\text{S}$ intermolecular contacts less than 3.75 Å but the $\text{As} \cdots \text{C}$ distances range from 3.32(1) to 3.63(1) Å for the six atoms in the phenyl ring. Similar interactions have been observed in some antimony adducts, viz. $2\text{SbCl}_3 \cdot \text{C}_6\text{H}_4\text{Me}_2$,¹² $2\text{SbCl}_3 \cdot \text{C}_{10}\text{H}_8$,¹³ $2\text{SbCl}_3 \cdot \text{C}_{12}\text{H}_{10}$,¹⁴ and $2\text{SbCl}_3 \cdot \text{NHPH}_2$.¹⁵ The geometry of the $\text{SbCl}_3 \cdots \text{Ph}$ group can be categorised by calculating a least-squares plane through the phenyl ring. Projections onto this plane (see Figures in refs. 12–15) show some small variations in orientation, particularly in whether the antimony atom is over the centre of the ring^{14,15} or towards one end,^{12,13} but these are not sufficiently different to suggest that there are two different types of interaction.

Despite this, two alternative explanations for the short $\text{Sb} \cdots \text{C}$ distances have been put forward. For the p -xylene¹² and naphthalene¹³ adducts the authors suggest that the geometry can be described in terms of a trigonal bipyramid obtained via sp^3d hybridisation for the antimony, with one chlorine and the benzene ring in axial sites and two chlorines and a lone pair in equatorial sites. The alternative description for the biphenyl¹⁴ and diphenylamine¹⁵ adducts states that the geometry is distorted octahedral, the metal being strongly bound to three chlorine atoms in a *fac* arrangement. The co-ordination sphere is completed by two chlorine atoms at *ca.* 3.4 Å and a lone pair/benzene ring.

The geometry of (1) (see Figure 2) more closely resembles the p -xylene and naphthalene structures, with the metal to one end of the ring. However as the interaction in (1) is between equivalent molecules of $\text{AsCl}(\text{tdt})$ packing effects will be much more important than for the SbCl_3 adducts where two different molecules are involved. Therefore we cannot draw any conclusions about the electronic nature of the interaction between the arsenic atom and the benzene ring. However in view of the occurrence of this interaction in several structures

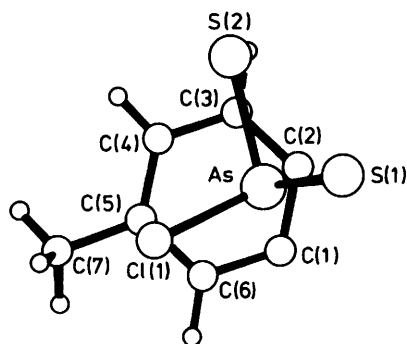


Figure 2. Projection of the AsClS_2 moiety of (1) onto the plane of the phenyl ring in the adjacent molecule

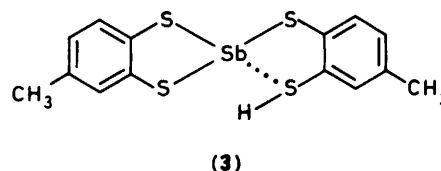
we believe that there is a weak π interaction between the metal and the benzene ring.

1:2 Addition.—With AsCl_3 no discrete complex was isolated. Reactions involving the direct addition of $\text{AsCl}_3:\text{H}_2\text{tdt}$ in a 1:2 molar ratio repeatedly gave yellow solids with various and inconclusive analytical data. In the case of SbCl_3 a deep yellow complex, (3), was isolated, which surprisingly, proved to be neutral due to retention of one of the thiol (SH) protons. The complex previously isolated by Wandiga⁵ from a similar 1:2 stoichiometric reaction was assigned a four-co-ordinate structure based on $\text{H}[\text{Sb}(\text{tdt})_2]\cdot\text{H}_2\text{O}$.

The i.r. spectrum of (3) shows a prominent $\nu(\text{S-H})$ single band at 2335 cm^{-1} . The ^1H n.m.r. spectrum shows a S-H singlet at δ 3.49 and a methyl singlet at δ 2.28 with an exact 1:6 integral ratio; the aromatic proton region is essentially unchanged with respect to that of the free ligand. The fact that the $\nu(\text{S-H})$ band has shifted (-210 cm^{-1}) to lower energy could be the result of a weak $\text{Sb}\cdots\text{S(H)}$ interaction (as shown) and/or some contribution from intermolecular hydrogen bonding. There are several possibilities concerning the structure and geometry of (3), e.g. tetrahedral, trigonal bipyramidal, or square pyramidal, depending on the presence, or otherwise, of a stereochemically active lone pair. Crystals suitable for an X-ray structure determination have proved elusive so far.

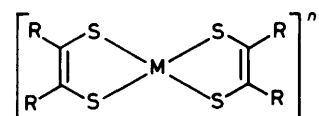
Removal of the remaining (SH) proton was effected by the addition of base (1 mol) but rather than the expected $[\text{Sb}^{\text{III}}(\text{tdt})_2]^-$, the deep purple-violet $[\text{Sb}^{\text{V}}(\text{tdt})_3]^-$ was obtained (see later).

The Bi^{III} complex was obtained as $[\text{NEt}_3\text{H}][\text{Bi}(\text{tdt})_2]$ following the addition of triethylamine (1 mol) to a 1:2 mixture of $\text{BiCl}_3\cdot\text{H}_2\text{tdt}$ in methanol solution. Both the ^1H n.m.r. and i.r. spectra confirm the absence of (SH) protons. Evidently methyl groups associated with the anion are equivalent and appear as a sharp singlet at δ 2.20. Formulation of this anionic Bi^{III} species as a monomeric four-co-ordinate compound is mere speculation and must be treated with reservation. The recent structure determination by Hunter and Weakley¹⁶ of the 1,2-dithiolato-complex $[\text{AsPh}_4][\text{Bi}\{\text{S}_2\text{C}_2(\text{CN})_2\}_2]$ reveals a linear polymeric chain structure in which adjacent bismuth centres are bridged by two dithiolene ligands, with each ligand providing one bridging sulphur atom. Although the Bi^{III} geometry begs precise description, the authors favour a distorted pentagonal bipyramidal AX_6E situation in which one of the equatorial positions is occupied by a stereochemically active lone pair. They also go on to propose by implication, similar polymeric structures for the related 1,2-dithiolato-anionic complexes $[\text{Bi}_2\{\text{S}_2\text{C}_2(\text{CN})_2\}_2\text{X}_4]^{2-}$ and $[\text{Bi}_2\{\text{S}_2\text{C}_2(\text{CN})_2\}_3\text{X}_2]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) reported earlier;² the possibility that our complex $[\text{NEt}_3\text{H}][\text{Bi}(\text{tdt})_2]$ can be added to the list is being investigated.



1:3 Addition.—The conversion of yellow $[\text{Sb}^{\text{III}}(\text{Htdt})(\text{tdt})]$ to the deep violet-purple anion $[\text{Sb}^{\text{V}}(\text{tdt})_3]^-$ has been mentioned above. This Sb^{V} species can be obtained directly from SbCl_3 or, if necessary, from antimony potassium tartrate. Addition of NEt_3 to a methanol solution of H_2tdt followed by dropwise addition of SbCl_3 or antimony potassium tartrate (1:1:1) at 273 K provides a deep purple solution of the $[\text{Sb}^{\text{V}}(\text{tdt})_3]^-$ anion which can be precipitated by large cations such as $[\text{NEt}_4]^+$ or $[\text{PPh}_4]^+$. The i.r. spectrum of $[\text{NEt}_4][\text{Sb}(\text{tdt})_3]$ confirms the complete removal of SH protons and shows the characteristic bands of the tetraethylammonium cation. The ^1H n.m.r. spectrum contains a sharp singlet at δ 2.22 for equivalent methyl groups of the anion and multiplets at δ 6.71 and 7.25 for aromatic ring protons; tetraethylammonium cation signals are observed at δ 1.07 (t, CH_3CH_2) and 2.93 (q, CH_3CH_2). A similar spectral pattern is observed for the PPh_4^+ complex. An X-ray crystal structure determination of $[\text{PPh}_4][\text{Sb}^{\text{V}}(\text{tdt})_3]$ (2) confirms the anticipated octahedral geometry of the anion, cf. the tris(benzene-1,2-diolato)arsenate(v) anion.¹⁷

1,2-Dithiolene complexes of the general type shown below



($\text{R} = \text{CN}, \text{Ph}, \text{or } \text{CF}_3$; $\text{M} = \text{transition or post-transition metal}$; $n = 0-2$) undergo reversible and facile step-wise electron-transfer reactions which may be brought about chemically and/or electrochemically and which represent a useful synthetic tool.¹⁸ Typically the violet Sb^{V} complex obtained from SbCl_3 and 1,2-dithiolene is an example of this characteristic redox be-

haviour.¹⁹ The present reaction involving $\text{SbCl}_3\text{-H}_2\text{tdt} \xrightarrow{\text{air}(\text{O}_2)} [\text{Sb}^{\text{V}}(\text{tdt})_3]^-$ provides another such example from Group 5B, with aerial oxidation responsible for $\text{Sb}^{\text{III}} \rightarrow \text{Sb}^{\text{V}}$. Why the addition of base to $[\text{Sb}(\text{Htdt})(\text{tdt})]$ provides us with this particular Sb^{V} anion, however, and not the Sb^{III} species $[\text{Sb}(\text{tdt})_2]^-$ remains an enigma. The existence of a four-co-ordinate $[\text{Sb}(\text{tdt})_2]^-$ anion analogous to the 1,2-dioxolato-complex, potassium bis(*o*-phenylenedioxy)arsenate(III)²⁰ (the structure approximates to a distorted trigonal bipyramid with the lone pair occupying an equatorial position) and similarly oxygen-bonded Sb^{III} complexes, e.g., antimony potassium tartrate,²¹ seems eminently reasonable. However, to our consternation we have been unable to isolate $[\text{Sb}^{\text{III}}(\text{tdt})_2]^-$ even though it, and the As^{III} and Bi^{III} counterparts have been reported previously.⁴

Crystal Structure of $[\text{PPh}_4][\text{Sb}(\text{tdt})_3]$ (2).—The structure of (2) consists of discrete $[\text{PPh}_4]^+$ cations and $[\text{Sb}(\text{tdt})_3]^-$ anions in general positions. The anion is illustrated in Figure 3 together with the atomic numbering scheme. As discussed above, there was some doubt as to the positions of the methyl groups on the tdt ligands and the atoms shown are those with the greatest population parameter.

The Sb atom is six-co-ordinate with Sb-S distances ranging from 2.34(3) to 2.50(2) Å. The *cis* angles subtended at the metal are all within 8.1° of 90° indicating that the geometry around the

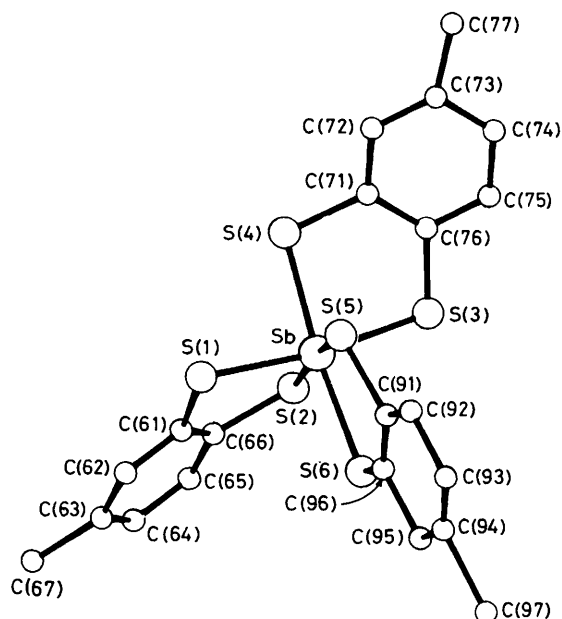


Figure 3. The structure of the $[\text{Sb}(\text{tdt})_3]^-$ anion of (2)

metal is as close to octahedral as the ligand bites permit. Indeed the structure is very similar to that of the tris(benzene-1,2-diolato)arsenate(v) anion.¹⁷

A search of the Cambridge Data Centre files shows a dozen or so other structures with SbS_6 cores but all, bar one, contain Sb^{III} in which the lone pair is stereochemically active. As a result none of these compounds has octahedral geometry. The only comparable Sb^{V} structure is tris(benzene-1,2-dithiolato)-antimonate(v)²² which has only been reported briefly and no co-ordinates are available.

The mean Sb-S distance in (2) is 2.44 Å with variations of up to 0.10 Å but we were unable to correlate these differences with any angle variations.

It is interesting to note that all the Sb^{III} structures in which there is clear evidence of an active lone pair contain small four-membered chelate rings. By contrast the present Sb^{V} compound contains five-membered rings. This trend is consistent with the theory that 'small-bite' bidentate ligand binding is synonymous with lone-pair activity. It seems clear also that the stability of the Sb^{V} ion is enhanced by the five-membered chelate rings.

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