Phenylantimony(V) Oxalates: Isolation and Crystal Structures of $[SbPh_4][SbPh_2(ox)_2]$, $[SbPh_3(OMe)]_2ox$ and $(SbPh_4)_2ox$†

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The course of the reaction between triphenylantimony dichloride and silver oxalate depends on both the solvent and temperature at which the reaction is carried out. No reaction occurs in toluene at room temperature, but on refluxing the solution, crystals of $[SbPh_4][SbPh_2(ox)_2]$ **1** [ox = oxalate(2−)], an ionic form of $SbPh_3(ox)$, are obtained. Covalent $SbPh_3(ox)$, on the other hand, is probably the initial product of reaction in methanol at room temperature, but on recrystallisation from hot methanol, crystals of a methoxy derivative, $[SbPh_3(OMe)]_2ox$ **2**, are obtained. Structures have been determined for both compounds. Compound **1** consists of tetrahedral $[SbPh_4]^+$ cations and octahedral $[SbPh_2(ox)_2]^-$ anions containing two chelating oxalate groups and phenyl groups in *cis* positions. The methoxy derivative **2** is centrosymmetric, with a quadridentate oxalate group and each antimony octahedrally co-ordinated to three phenyl groups, one methoxy group and two oxygens from the oxalate group. A quadridentate oxalate group is also present in $(SbPh_4)_2ox$ **3**, obtained from $[SbPh_4]Br$ and silver oxalate. The structure contains two essentially identical, independent, centrosymmetric molecules with antimony again in distorted-octahedral co-ordination.

Our interest in investigating antimony(V) oxalates stems from the possibility of the oxalate group stabilising a five-co-ordinate square-pyramidal, rather than the more usual trigonal-bipyramidal, geometry at antimony. Incorporation of dioxo chelating groups into a series of organo-phosphorus and -arsenic derivatives has been used successfully, among others, by Holmes and co-workers[1] to promote stabilisation of such square-pyramidal geometry. Comparable examples are much rarer in antimony chemistry but, in addition to $SbPh_5$,[2] one of the antimony atoms in $[SbPh_3(cat)]_2 \cdot H_2O$ (H_2cat = catechol) shows square-pyramidal geometry.[3]

Triphenylantimony oxalate itself has been reported as a white solid melting at 160–161 °C obtained from the metathesis reaction between $SbPh_3Cl_2$ and silver oxalate in methanol.[4] On the basis of its solubility properties and the similarity of its IR spectrum with that of the corresponding trimethyl derivative, the authors consider that the oxalate group bridges between pairs of antimony atoms. On these spectroscopic grounds alone it does not seem possible to rule out an alternative monomeric trigonal-bipyramidal structure where the oxalate group chelates between equatorial and axial positions.

In addition to being a strong chelating and bridging ligand, the oxalate group can also show quadridentate behaviour, where all four oxygens are involved in bonding. This mode of co-ordination has been confirmed in a range of both transition-metal[5] and main-group-element oxalates.[6–10]

Experimental

Silver oxalate $Ag_2(ox)$ was prepared from silver nitrate and sodium oxalate in aqueous solution; after filtration, the white solid was dried in a vacuum over phosphorus pentaoxide.

Reaction of Triphenylantimony Dichloride with Silver Oxalate.—(*a*) *In refluxing toluene.* Triphenylantimony dichloride (4.2 g, 0.01 mol) and silver oxalate (3.03 g, 0.01 mol) were refluxed in dry toluene for 9 h. Filtration of the solution followed by slow cooling yielded white crystals of $[SbPh_4]$-$[SbPh_2(ox)_2]$ **1**. Yield 1.9 g (45%), m.p. 198–199 °C (Found: C, 54.6; H, 3.9. Calc. for $C_{20}H_{15}O_4Sb$: C, 54.5; H, 3.4%).

(*b*) *In methanol at room temperature.* Triphenylantimony dichloride (6.0 g, 0.014 mol) and silver oxalate (4.3 g, 0.014 mol) were shaken in methanol (250 cm^3) for 24 h at room temperature. After filtration, the volume of the mother-liquor was reduced to *ca.* 20 cm^3 and the white crystals of $[SbPh_3(OMe)]_2ox$ **2** which separated were recrystallised from methanol. Further product could be obtained by extracting the silver residues with hot methanol. Yield 3.8 g (63%), m.p. 265 °C (Found: C, 55.5; H, 4.1. Calc. for $C_{20}H_{15}O_4Sb$: C, 54.5; H, 3.4. Calc. for $C_{40}H_{36}O_6Sb_2$: C, 56.1; H, 4.2%).

Preparation of Bis(tetraphenylantimony) Oxalate.—Tetraphenylantimony bromide[11] (3.0 g, 5.88 mmol) was shaken for 72 h in toluene (300 cm^3) with silver oxalate (0.82 g, 2.70 mmol). Following filtration, the solution volume was reduced to *ca.* 15 cm^3 and on standing white crystals of the product **3** were obtained. Yield 2.0 g (79%), m.p. 235 °C (lit.,[12] 237 °C) (Found: C, 63.1; H, 4.4. Calc. for $C_{50}H_{40}O_4Sb_2$: C, 63.4; H, 4.3%).

Crystal Structure of $[SbPh_4][SbPh_2(ox)_2]$ **1**.—*Crystal data.* $C_{40}H_{30}O_8Sb_2$, M = 882.2, monoclinic, space group $P2_1/c$, a = 12.617(3), b = 17.175(3), c = 16.881(3) Å, β = 107.98(4)°, U = 3479.4 Å^3, Z = 4, D_c = 1.68 g cm^{-3}, $F(000)$ = 1744, Mo-Kα radiation, λ = 0.7107 Å, μ(Mo-Kα) = 21.2 cm^{-1}.

Structure determination. Crystals suitable for X-ray analysis were obtained by slowly cooling a solution of the compound in toluene. Data were collected for 4686 reflections using a Hilger and Watts four-circle diffractometer fitted with a graphite monochromator. Of these, 4297 with $I > 3\sigma(I)$ were considered to be observed and were corrected for Lorentz and polarisation effects. Crystallographic calculations used the CRYSTALS programs[13] and scattering factors for neutral atoms.[14] Density calculation implied that the asymmetric unit contained two $Ph_3Sb(ox)$ units and possible positions for the two antimony atoms were obtained from a three-dimensional Patterson synthesis. Successive Fourier difference syntheses revealed

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Fractional atomic coordinates (× 10^4), with estimated standard deviations (e.s.d.s) in parentheses, for $[SbPh_4][SbPh_2(ox)_2]$ **1**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb(1)	984.4(3)	2 917.3(2)	2 894.9(3)	Sb(2)	6 115.9(3)	2 747.8(2)	7 903.5(2)
C(11)	−392(5)	3 645(4)	2 383(4)	O(1)	7 398(3)	2 989(2)	7 455(2)
C(12)	−1 163(6)	3 429(4)	1 665(5)	O(2)	6 858(3)	3 673(2)	8 660(2)
C(13)	−2 089(7)	3 888(5)	1 314(5)	C(1)	7 946(5)	3 640(4)	7 724(4)
C(14)	−2 217(6)	4 564(4)	1 677(5)	C(2)	7 630(5)	4 049(4)	8 428(4)
C(15)	−1 480(8)	4 788(5)	2 397(6)	O(11)	8 658(4)	3 891(3)	7 453(3)
C(16)	−550(8)	4 324(5)	2 761(5)	O(12)	8 027(4)	4 657(3)	8 708(3)
C(21)	1 280(5)	2 296(4)	1 918(4)	O(3)	5 315(3)	3 669(2)	7 161(3)
C(22)	601(5)	1 670(4)	1 559(4)	O(4)	4 816(3)	2 929(2)	8 352(2)
C(23)	826(7)	1 272(4)	906(4)	C(3)	4 481(5)	3 977(4)	7 353(4)
C(24)	1 706(6)	1 498(4)	634(4)	C(4)	4 190(5)	3 531(4)	8 056(4)
C(25)	2 350(6)	2 124(5)	999(4)	O(13)	3 961(4)	4 533(3)	7 029(3)
C(26)	2 134(5)	2 519(4)	1 637(4)	O(14)	3 426(4)	3 726(3)	8 297(3)
C(31)	695(5)	2 182(4)	3 791(4)	C(51)	5 361(5)	1 981(3)	6 904(3)
C(32)	1 336(6)	1 519(4)	4 039(4)	C(52)	5 363(5)	2 158(4)	6 107(4)
C(33)	1 155(6)	1 047(4)	4 648(5)	C(53)	4 858(6)	1 666(5)	5 448(4)
C(34)	327(6)	1 235(4)	4 997(5)	C(54)	4 334(6)	1 007(5)	5 599(5)
C(35)	−297(6)	1 891(5)	4 744(4)	C(55)	4 316(7)	830(5)	6 384(5)
C(36)	−129(5)	2 376(4)	4 135(4)	C(56)	4 825(6)	1 328(4)	7 043(4)
C(41)	2 394(5)	3 605(4)	3 422(4)	C(61)	6 860(5)	1 963(3)	8 889(3)
C(42)	3 226(6)	3 314(4)	4 090(4)	C(62)	7 002(5)	2 166(4)	9 711(4)
C(43)	4 196(6)	3 740(5)	4 411(5)	C(63)	7 440(6)	1 632(5)	10 336(4)
C(44)	4 322(6)	4 439(4)	4 061(4)	C(64)	7 739(7)	904(5)	10 155(5)
C(45)	3 489(7)	4 722(4)	3 408(5)	C(65)	7 599(7)	705(4)	9 336(5)
C(46)	2 513(7)	4 310(5)	3 075(5)	C(66)	7 159(6)	1 236(4)	8 704(4)

Table 2 Fractional atomic coordinates (× 10^4), with e.s.d.s in parentheses, for $[SbPh_3(OMe)]_2ox$ **2**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb(1)	3298.4(3)	2398.5(3)	2576.4(3)
O(1)	2031(4)	2296(4)	793(3)
O(2)	6454(4)	5180(3)	6488(3)
O(3)	4865(4)	3191(3)	4725(3)
C(1)	799(7)	2849(6)	553(5)
C(2)	5381(5)	4535(4)	5353(4)
C(11)	5630(6)	3697(5)	2422(4)
C(12)	7042(6)	3481(6)	2968(5)
C(13)	8558(7)	4296(7)	2849(6)
C(14)	8658(7)	5306(7)	2174(6)
C(15)	7261(8)	5528(6)	1622(6)
C(16)	5746(7)	4717(5)	1742(5)
C(21)	3459(5)	327(4)	2235(4)
C(22)	3330(7)	−414(5)	3159(5)
C(23)	3388(7)	−1782(6)	2945(7)
C(24)	3545(7)	−2415(6)	1781(7)
C(25)	3673(7)	−1683(6)	872(6)
C(26)	3643(6)	−305(5)	1088(5)
C(31)	1151(6)	1690(5)	3162(4)
C(32)	1065(6)	2277(6)	4368(5)
C(33)	−400(7)	1627(7)	4619(6)
C(34)	−1768(7)	403(7)	3679(6)
C(35)	−1690(6)	−188(6)	2476(5)
C(36)	−255(6)	454(5)	2222(5)

positions for the other non-hydrogen atoms. Refinement by full-matrix least squares with isotropic thermal parameters converged at *R* 0.069 and at 0.038 after refinement with anisotropic thermal parameters, placement of hydrogen atoms at the calculated positions [*d*(C–H) = 1.0 Å] and application of a four-coefficient Chebyshev weighting scheme. Except in the vicinity of the heavy atoms, there were no peaks in a final Fourier difference synthesis with intensities >0.3 e Å^{-3}. An absorption correction was not considered to be necessary. The final atomic coordinates are listed in Table 1.

Crystal Structure of $[SbPh_3(OMe)]_2ox$ **2**.—*Crystal data.* $C_{40}H_{36}O_6Sb_2$, *M* = 856.2, triclinic, space group $P\bar{1}$, $a = 9.051(2)$, $b = 10.155(2)$, $c = 11.015(3)$ Å, $\alpha = 101.11(4)$, $\beta = 105.68(4)$, $\gamma = 110.69(5)°$, $U = 863.8$ Å^3, $Z = 1$, $D_c = 1.64$ g cm^{-3}, *F*(000) = 426, Mo-Kα radiation, $\lambda = 0.7107$ Å, μ(Mo-Kα) = 21.2 cm^{-1}.

Structure determination. Data were measured for 3296 reflections of which 2778 were observed and corrected as described above. The position of the antimony in the asymmetric unit was obtained from a three-dimensional Patterson synthesis and the structure was solved and refined as described above. The *R* value converged at 0.069 with isotropic thermal parameters and at 0.032 with anisotropic parameters, the hydrogens placed at the calculated positions and application of a four-coefficient Chebyshev weighting scheme. Final values for the atomic coordinates are listed in Table 2.

Crystal Structure of $(SbPh_4)_2ox$ **3**.—*Crystal data.* $C_{50}H_{40}O_4Sb_2$, *M* = 948.4, triclinic, space group $P\bar{1}$, $a = 9.647(2)$, $b = 10.314(2)$, $c = 23.033(5)$ Å, $\alpha = 95.85(4)$, $\beta = 96.65(4)$, $\gamma = 114.46(4)°$, $U = 2043.6$ Å^3, $Z = 2$, $D_c = 1.53$ g cm^{-3}, *F*(000) = 948, Mo-Kα radiation, $\lambda = 0.7107$ Å, μ(Mo-Kα) = 21.2 cm^{-1}.

Structure determination. Data were measured for 7013 reflections of which 6374 were observed and corrected as described above. An absorption correction was not considered necessary. The pattern of peaks in the Patterson map showed that the asymmetric unit contained two independent antimony atoms and gave possible positions for them. The structure was solved and refined as described above to show the presence of two independent centrosymmetric molecules. The *R* value converged at 0.076 with isotropic thermal parameters and at 0.036 with anisotropic parameters, the hydrogens placed at the calculated positions and application of a four-coefficient Chebyshev weighting scheme. Except in the vicinity of the heavy atoms there were no peaks in a final Fourier difference map with heights greater than 0.3 e Å^{-3}. Final values for the atomic coordinates are listed in Table 3.

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

Results

Preparation of Compounds.—The preparation of triphenyl-

Table 3 Fractional atomic coordinates (× 10^4), with e.s.d.s in parentheses, for $(SbPh_4)_2ox$ **3**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Sb(1)	2365.8(4)	1603.1(4)	1103.3(1)	Sb(2)	1426.8(4)	2250.4(4)	6089.8(1)
O(1)	−189(4)	936(4)	641(2)	O(2)	723(4)	−178(4)	5703(1)
O(3)	−1978(4)	−452(4)	−127(2)	O(4)	−2(4)	−1700(4)	4857(2)
C(1)	−626(6)	130(6)	150(2)	C(2)	211(6)	−533(5)	5165(2)
C(11)	4709(6)	1853(6)	1250(2)	C(51)	1702(6)	4430(6)	6176(2)
C(12)	5678(7)	2577(7)	1773(3)	C(52)	2968(9)	5574(7)	6516(3)
C(13)	7221(7)	2781(7)	1851(3)	C(53)	3119(11)	6959(7)	6564(3)
C(14)	7742(7)	2219(7)	1396(3)	C(54)	1987(11)	7241(7)	6249(3)
C(15)	6790(7)	1478(8)	885(3)	C(55)	731(9)	6118(8)	5885(4)
C(16)	5240(6)	1279(7)	798(3)	C(56)	568(8)	4724(7)	5859(3)
C(21)	1257(6)	−611(6)	1231(2)	C(61)	3241(7)	2524(6)	5575(3)
C(22)	−109(7)	−1105(7)	1456(3)	C(62)	3286(8)	3129(7)	5076(3)
C(23)	−805(8)	−2533(8)	1559(3)	C(63)	4524(9)	3357(8)	4767(3)
C(24)	−176(10)	−3447(8)	1434(3)	C(64)	5688(10)	3009(9)	4979(4)
C(25)	1212(9)	−2957(7)	1210(3)	C(65)	5673(10)	2443(11)	5474(4)
C(26)	1913(8)	−1533(7)	1109(3)	C(66)	4409(9)	2164(10)	5777(3)
C(31)	2834(7)	3483(6)	694(2)	C(71)	2524(6)	1941(6)	6892(2)
C(32)	1847(9)	3695(8)	273(3)	C(72)	3968(7)	2921(7)	7217(3)
C(33)	2322(11)	5022(9)	65(3)	C(73)	4602(8)	2579(9)	7714(3)
C(34)	3759(11)	6114(9)	269(3)	C(74)	3843(9)	1248(9)	7885(3)
C(35)	4753(9)	5934(8)	687(3)	C(75)	2422(9)	262(8)	7557(3)
C(36)	4286(8)	4610(7)	896(3)	C(76)	1782(7)	621(7)	7078(2)
C(41)	2161(6)	2532(6)	1950(2)	C(81)	−837(6)	1412(5)	6335(2)
C(42)	1890(7)	3741(6)	2006(3)	C(82)	−857(7)	2088(6)	6889(3)
C(43)	1801(9)	4346(8)	2565(4)	C(83)	−2250(7)	1679(7)	7107(3)
C(44)	1996(9)	3727(9)	3058(3)	C(84)	−3572(7)	654(7)	6781(3)
C(45)	2243(9)	2548(8)	3005(3)	C(85)	−3565(7)	−20(7)	6226(3)
C(46)	2312(8)	1917(7)	2442(3)	C(86)	−2175(7)	364(7)	6010(3)

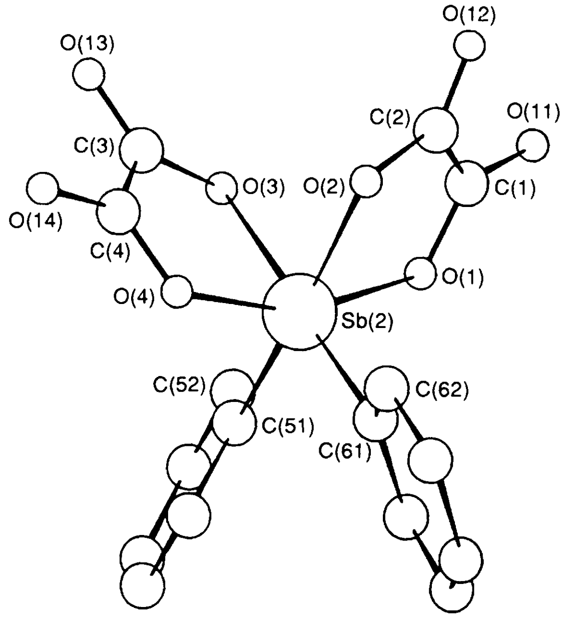

Fig. 1 Structure of the $[SbPh_2(ox)_2]^-$ anion in compound **1**, showing the atom numbering scheme

antimony oxalate has been repeated and shown to be more complicated than initially reported.[4] Our first reactions used toluene as the solvent, as there are indications that compounds containing Sb–O–Sb bonds react to give methoxy derivatives in methanol solution.[15] At room temperature in toluene there was, however, no reaction between $SbPh_3Cl_2$ and silver oxalate, but at reflux a white solid was obtained, which analysed as the expected oxalate. However, both the melting point (198–199 °C compared with 160–161 °C) and IR spectrum were different from those reported by Goel *et al.*[4] Our product showed new bands at 1720, 1660, 1320, 1300 and 790 cm^{-1}, and the mass spectrum contained a prominent peak associated with the $[SbPh]_4{}^+$ ion. The course of the reaction was followed by periodically withdrawing aliquots of the solution and recording the IR spectrum, but there was no evidence for the formation of any intermediate compound.

When the reaction was carried out in methanol the initial product had the same IR spectrum (oxalate bands at 1740vs, 1655vs, 1360s, 1210s, 980m and 780/760s cm^{-1}) as that reported previously[4] with the two highest-energy bands implying the presence of C=O groups. Attempts to recrystallise the initial product from methanol led to a product with a markedly changed IR spectrum (bands at 1630s, 1570s, 1070w, 790s and 520m cm^{-1}). Lowering of the high-energy oxalate bands implies a substantial reduction in the formal C=O bond order, which could arise either by formation of an oxalate ion or if the group participated in further bonding, for example, as a quadridentate ligand. In addition the IR spectrum contains a broad band at *ca.* 2920 cm^{-1}, suggesting the presence of a methyl group from reaction with the solvent. This was confirmed by mass spectrometry, which showed peaks that could be assigned to $Ph_3Sb(OMe)$, $Ph_2Sb(OMe)$ and $PhSb(OMe)$ ions.

To resolve problems in the identification of the two compounds, X-ray crystallographic studies were carried out.

Tetraphenylantimony oxalate is reported[12] to be monomeric in benzene and a weak electrolyte in nitromethane solution. Its IR spectrum contains no oxalate absorption higher than 1630 cm^{-1}, suggesting that the oxalate here is also quadridentate. The spectrum of our product, which shows bands at 1525 and 1070 cm^{-1} in addition to those reported in the earlier paper, is very similar to that of the methoxy-derivative **2** implying that the mode of bonding is also similar.

Structure of Compound **1**.—The structure determination shows that the compound is ionic, consisting of a tetrahedral tetraphenylantimony(V) cation and an octahedral dioxalatodiphenylantimony(V) anion. Important bond distances and angles for the compound are summarised in Table 4 and a diagram of the structure with the atom numbering scheme is in Fig. 1.

As expected, the Sb–C distances in the cation are equal

Table 4 Selected bond distances (Å) and angles (°), with e.s.d.s in parentheses, for $[SbPh_4][SbPh_2(ox)_2]$ **1**

Sb(1)–C(11)	2.098(7)	O(1)–Sb(2)–O(2)	79.2(2)
Sb(1)–C(21)	2.092(6)	O(1)–Sb(2)–O(3)	85.1(2)
Sb(1)–C(31)	2.088(6)	O(1)–Sb(2)–O(4)	159.4(2)
Sb(1)–C(41)	2.091(6)	O(1)–Sb(2)–C(51)	92.5(2)
		O(1)–Sb(2)–C(61)	102.2(2)
C(11)–Sb(1)–C(21)	107.8(2)	O(2)–Sb(2)–O(3)	80.3(2)
C(11)–Sb(1)–C(31)	110.6(2)	O(2)–Sb(2)–O(4)	85.2(2)
C(11)–Sb(1)–C(41)	109.0(2)	O(2)–Sb(2)–C(51)	166.7(2)
C(21)–Sb(1)–C(31)	112.1(2)	O(2)–Sb(2)–C(61)	89.9(2)
C(21)–Sb(1)–C(41)	106.8(2)	O(3)–Sb(2)–O(4)	79.1(2)
C(31)–Sb(1)–C(41)	110.5(2)	O(3)–Sb(2)–C(51)	88.7(2)
		O(3)–Sb(2)–C(61)	166.5(2)
Sb(2)–O(1)	2.029(4)	O(4)–Sb(2)–C(51)	100.1(2)
Sb(2)–O(2)	2.072(4)	O(4)–Sb(2)–C(61)	91.0(2)
Sb(2)–O(3)	2.077(4)	C(51)–Sb(2)–C(61)	102.2(2)
Sb(2)–O(4)	2.032(4)		
Sb(2)–C(51)	2.120(6)		
Sb(2)–C(61)	2.122(5)		
C(1)–O(1)	1.318(7)	C(3)–O(3)	1.306(7)
C(1)–O(11)	1.207(7)	C(3)–O(13)	1.191(8)
C(1)–C(2)	1.535(8)	C(3)–C(4)	1.548(9)
C(2)–O(2)	1.324(7)	C(4)–O(4)	1.304(7)
C(2)–O(12)	1.192(7)	C(4)–O(14)	1.204(7)
Sb(2)–O(1)–C(1)	116.0(4)	Sb(2)–O(3)–C(3)	116.0(4)
Sb(2)–O(2)–C(2)	115.2(4)	Sb(2)–O(4)–C(4)	116.2(4)
C(2)–C(1)–O(1)	114.9(5)	C(4)–C(3)–O(3)	112.9(5)
C(2)–C(1)–O(11)	122.1(6)	C(4)–C(3)–O(13)	121.5(6)
O(1)–C(1)–O(11)	123.0(6)	O(3)–C(3)–O(13)	125.6(6)
C(1)–C(2)–O(2)	113.3(5)	C(3)–C(4)–O(4)	115.4(5)
C(1)–C(2)–O(12)	122.1(6)	C(3)–C(4)–O(14)	121.7(6)
O(2)–C(2)–O(12)	124.6(6)	O(4)–C(4)–O(14)	122.9(6)

Table 5 Selected bond distances (Å) and angles (°), with e.s.d.s in parentheses, for $[SbPh_3(OMe)]_2ox$ **2**

Sb(1)–O(1)	1.950(3)	Sb(1)–C(31)	2.141(4)
Sb(1)–O(2′)*	2.380(3)	O(1)–C(1)	1.403(6)
Sb(1)–O(3)	2.214(3)	C(2)–O(2)	1.229(5)
Sb(1)–C(11)	2.129(4)	C(2)–O(3)	1.254(5)
Sb(1)–C(21)	2.128(4)	C(2)–C(2′)	1.558(8)
O(1)–Sb(1)–O(2)	91.8(1)	O(3)–Sb(1)–C(21)	93.6(1)
O(1)–Sb(1)–O(3)	163.6(1)	O(3)–Sb(1)–C(31)	86.0(1)
O(1)–Sb(1)–C(11)	90.7(1)	C(11)–Sb(1)–C(21)	98.3(2)
O(1)–Sb(1)–C(21)	102.5(2)	C(11)–Sb(1)–C(31)	163.2(2)
O(1)–Sb(1)–C(31)	95.7(2)	C(21)–Sb(1)–C(31)	95.5(2)
O(2′)–Sb(1)–C(11)	72.1(1)	Sb(1)–O(1)–C(1)	122.2(3)
O(2′)–Sb(1)–C(11)	80.4(1)	Sb(1)–O(3)–C(2)	117.7(3)
O(2′)–Sb(1)–C(21)	165.7(1)	Sb(1)–O(2′)–C(2′)	113.2(2)
O(2′)–Sb(1)–C(31)	83.9(1)	O(2)–C(2)–O(3)	124.9(4)
O(3)–Sb(1)–C(11)	83.5(1)	O(2)–C(2)–C(2′)	117.4(4)

* Atoms carrying a prime are related to unprimed atoms by the symmetry operation $1 - x, 1 - y, 1 - z$.

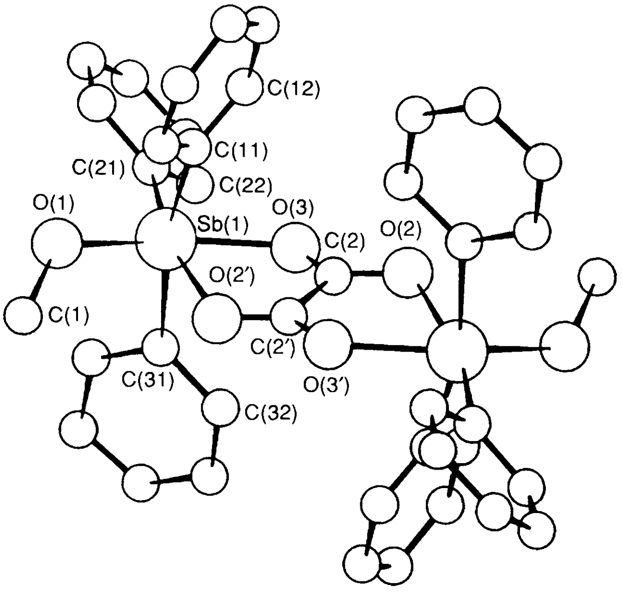

Fig. 2 Structure of $[SbPh_3(OMe)]_2ox$ **2**, showing the atom numbering scheme

(mean 2.09 Å) but the bond angles range between 106.8 and 112.1° (mean 109.4°). Phenyl groups in the anion, which is structurally similar to that in the complex product obtained from $(SbPh_2BrO)_2$ and silver oxalate,[16] occupy *cis* positions [C(51)–Sb(2)–C(61) 102.2°], with antimony–carbon bond distances of 2.12 Å, somewhat longer than those in the cation. Bonds to oxygen, on the other hand, fall into two groups of two (2.03 and 2.07 Å respectively), with the implication that the oxalate groups are slightly unsymmetrically co-ordinated. This difference is however not reflected in the related C–O separations. The two shorter Sb–O contacts, to O(1) and O(4) respectively, are *trans* to each other (159.4°), while the longer ones are *cis* (80.3°). These values give some indication of the distortion of the octahedron about Sb(2). Obviously further distortion results from the presence of chelating oxalate groups where the bite of the chelate reduces the angles at antimony to 79°. The carbon–oxygen distances in the co-ordinated oxalate groups, implying the presence of both single (1.31 Å) and double bonds (1.20 Å), support the infrared interpretation given above.

Both the phenyl and oxalate groups are effectively planar. In the C(1) oxalate group the maximum deviation from the best mean plane through the six atoms of the group is 0.03 Å [individual atom deviations are C(1) 0.02, O(1) 0.02, O(11) −0.02, C(2) −0.01, O(2) −0.02, O(12) 0.03 Å] with the antimony atom lying 0.29 Å from this plane. The C(3) group is more accurately planar (deviations from the best mean plane are less than 0.01 Å) and the antimony atom lies only 0.15 Å out of this plane.

Structure of Compound **2**.—Important distances and angles for compound **2** are listed in Table 5 and a diagram of the structure is given in Fig. 2. The results confirm the presence of a methoxy group in the product and show that compound **2** is, in fact, bis(methoxytriphenylantimony) oxalate. The molecule is centrosymmetric with basically octahedral geometry about antimony; the oxalate group is quadridentate. Consistent with previous work, the oxalate group co-ordinates to form two five-membered rings, rather than as the 'biacetate' alternative, which would lead to two highly strained four-membered rings. The three phenyl groups (and, of course, the three oxygen atoms) occupy meridional positions; there was no evidence for the alternative facial arrangement of substituents, which has been observed previously in triphenylantimony catecholate hemihydrate.[3]

Co-ordination about antimony in this compound is distorted octahedral to three phenyl groups (mean distance 2.13 Å), a methoxy group at 1.95 Å and two oxygen atoms. Antimony oxygen separations are 2.214 and 2.380 Å to O(3) and O(2) respectively, with the shorter contact *trans* to the methoxy group. The corresponding carbon–oxygen distances in the oxalate group are 1.254 and 1.229 Å. For comparison purposes, the carbon–oxygen separations in an ionic oxalate fall between 1.25 and 1.27 Å,[17] while in two pyridinium oxalate–oxalic acid adducts[18] the C–O distances in the oxalic acid molecule are distinctly different at *ca.* 1.20 and 1.30 Å respectively. The C–O bond lengths in quadridentate oxalates are variable, but the effectively equal distances found in a nickel complex[5] and two antimony compounds[6,7] are in the minority. In most cases,

Table 6 Selected bond distances (Å) and angles (°), with e.s.d.s in parentheses, for $(SbPh_4)_2$ox **3**

Molecule 1		Molecule 2	
Sb(1)–O(1)	2.349(3)	Sb(2)–O(2)	2.350(3)
Sb(1)–O(3′)*	2.346(3)	Sb(2)–O(4′)*	2.318(4)
Sb(1)–C(11)	2.148(5)	Sb(2)–C(51)	2.137(5)
Sb(1)–C(21)	2.153(6)	Sb(2)–C(61)	2.165(6)
Sb(1)–C(31)	2.144(6)	Sb(2)–C(71)	2.141(5)
Sb(1)–C(41)	2.152(5)	Sb(2)–C(81)	2.158(5)
C(1)–O(1)	1.248(6)	C(2)–O(2)	1.238(6)
C(1)–O(3)	1.245(6)	C(2)–O(4)	1.258(6)
C(1)–C(1′)	1.560(9)	C(2)–C(2′)	1.555(9)
O(1)–Sb(1)–O(3)	70.5(1)	O(2)–Sb(2)–O(4′)	70.8(2)
O(1)–Sb(1)–C(11)	161.1(2)	O(2)–Sb(2)–C(51)	162.2(2)
O(1)–Sb(1)–C(21)	78.8(2)	O(2)–Sb(2)–C(61)	80.2(2)
O(1)–Sb(1)–C(31)	83.2(2)	O(2)–Sb(2)–C(71)	88.4(2)
O(1)–Sb(1)–C(41)	96.3(2)	O(2)–Sb(2)–C(81)	84.1(2)
O(3′)–Sb(1)–C(11)	90.7(2)	O(4′)–Sb(2)–C(51)	91.4(2)
O(3′)–Sb(1)–C(21)	80.7(2)	O(4′)–Sb(2)–C(61)	80.4(2)
O(3′)–Sb(1)–C(31)	83.4(2)	O(4′)–Sb(2)–C(71)	159.2(2)
O(3′)–Sb(1)–C(41)	166.8(2)	O(4′)–Sb(2)–C(81)	82.7(2)
C(11)–Sb(1)–C(21)	97.7(2)	C(51)–Sb(2)–C(61)	96.7(2)
C(11)–Sb(1)–C(31)	95.9(2)	C(51)–Sb(1)–C(71)	109.4(2)
C(11)–Sb(1)–C(41)	102.5(2)	C(51)–Sb(2)–C(81)	94.5(2)
C(21)–Sb(1)–C(31)	159.1(2)	C(61)–Sb(2)–C(71)	98.0(2)
C(21)–Sb(1)–C(41)	96.1(2)	C(61)–Sb(2)–C(81)	159.9(2)
C(31)–Sb(1)–C(41)	96.3(2)	C(71)–Sb(2)–C(81)	94.0(2)
Sb(1)–O(1)–C(1)	116.3(3)	Sb(2)–O(2)–C(2)	115.3(3)
Sb(1)–O(3′)–C(1′)	116.8(3)	Sb(2)–O(4′)–C(2′)	116.6(3)
O(1)–C(1)–O(3)	125.0(4)	O(2)–C(2)–O(4)	125.1(5)
O(1)–C(1)–C(1′)	117.6(6)	O(2)–C(2)–C(2′)	118.2(5)

* Atoms carrying a prime are related to unprimed atoms by the symmetry operations $-x, -y, -z$ for molecule 1 and $-x, -y, 1 - z$ for molecule 2.

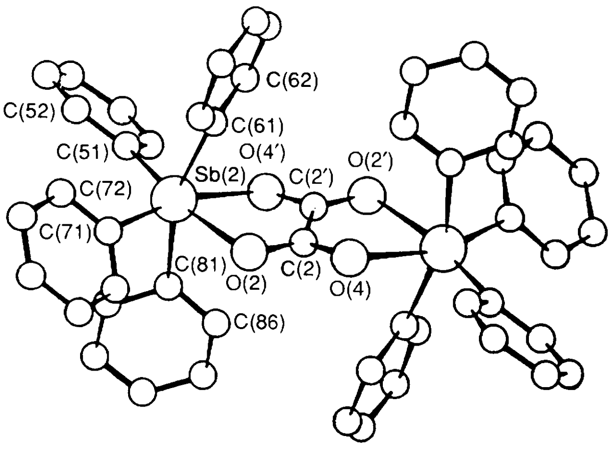

Fig. 3 Structure of molecule 2 in $(SbPh_4)_2$ox **3**, showing the atom numbering scheme

distances fall within the range 1.23–1.28 Å, implying that there is incomplete electron delocalisation within the group. Although an inverse correlation would be expected (and is found here) between the lengths of the related C–O and M–O bonds, this is not always observed and Curtis *et al.*[5] point out that the C–O distances in a co-ordinated oxalate are relatively insensitive to interactions by the oxygen atoms and are unlikely to reflect differences in donor bonding.

Other oxalate parameters conform to those generally observed with a 'long' C–C distance (1.558 Å) and O–C–O and O–C–C angles of 124.9 and 117.4°, respectively.

As expected, the greatest distortion from octahedral geometry about antimony is a consequence of the short bite of the oxalate group, which constrains the O(2)–Sb(1)–O(3) angle to 72.1°, comparable to that in compound **1**. In compensation, the C(21)–Sb(1)–O(1) angle increases to 102.5°. It is clear that the *trans* angles involving oxalate oxygens will be lower than the 180° ideal but it is surprising that the angle between the two *trans* phenyl groups is also reduced to 163.2°. Here the C(11) and C(31) phenyl groups are distorted towards the oxalate group.

Structure of Compound **3**.—Bond distances and angles for this compound are collected in Table 6 and the structure of the Sb(2) molecule is illustrated in Fig. 3. Each of the two independent, centrosymmetric molecules in the unit cell is octahedral but distorted as a consequence of the small bite of the oxalate group. The major molecular parameters are also similar but there are small differences in the co-ordination of the two oxalate groups. For example, the two Sb–O contacts at Sb(1) (2.349, 2.346 Å) and the C–O distances (1.248, 1.245 Å) are both effectively equal, while there are distinctly different Sb–O (2.318 and 2.350 Å) and C–O distances (1.258 and 1.238 Å) in the Sb(2) molecule. Although the inverse relationship between the Sb–O and C–O distances holds here, it is difficult to believe that there is any major difference in oxalate bonding in the two independent molecules.

As perhaps expected, distortions of the octahedral geometry about the central atoms here are comparable to those in compound **2**, and again the two *trans* phenyl groups are bent inwards towards the oxalate group.

Discussion

Isolation of an ionic form **1** of triphenylantimony oxalate from the $SbPh_3Cl_2$–silver oxalate reaction in refluxing toluene, rather than a five-co-ordinate monomer or an oxalate-bridged polymer, is unusual but covalent and ionic forms of the same compound are known. A number of examples are found in phosphorus chemistry,[19] and dimethylantimony trichloride, for example, can be obtained as both a doubly chloride-bridged covalent dimer and the ionic $[SbMe_4][SbCl_6]$.[20]

The present reaction requires redistribution of phenyl groups and it is tempting to consider that the first step is isomerisation of $SbPh_3Cl_2$ to $[SbPh_4][SbPh_2Cl_4]$. From separate experiments in boiling toluene there is no evidence for this specific process, but phenyl-group redistributions are observed in other phenylantimony systems, particularly with antimony(III), where they form the basis of low-temperature, high-yield syntheses of $SbPhX_2$ and $SbPh_2X$ for X = Cl or Br.[21] A number of plausible mechanisms can be suggested for the reaction in toluene, based on the formation of intermediates containing both bridging oxalate and phenyl groups.

An attractive first step in a possible mechanism is the formation of an oxalate-bridged species, where chlorine atoms from each of two molecules of the starting material are substituted by one oxalate group. Nucleophilic attack by an oxalate oxygen on one antimony atom and concurrent transfer of a phenyl group (*via* a phenyl-bridged intermediate) to the second antimony could follow, to give, respectively, $SbPh_4Cl$ and $SbPh_2Cl$(ox), as intermediates. A second bridging oxalate group could replace the remaining chlorine atoms and a similar nucleophilic attack would convert it into the second chelating group in the anion of the final product.

An alternative possibility to the formation of a second oxalate-bridged intermediate is the transfer of a chloride ion between antimony atoms, leading to ionic $[SbPh_4][SbPh_2Cl_2(ox)]$. Replacement of the two chlorine atoms by a second molecule of oxalate would then give the final product.

There is evidence that the initial product of the methanol reaction is covalent triphenylantimony oxalate, which subsequently reacts rapidly with the solvent. If the oxalate has a trigonal-bipyramidal structure, methanol would attack preferentially between the two equatorial phenyl groups, which would become the *trans* phenyl groups in the final product. During the process, one molecule of oxalic acid would be released for each pair of antimony atoms and the remaining oxalate group would become quadridentate. On the other hand, if the initial product is not $SbPh_3(ox)$, it is possible to postulate formation of the same oxalate-bridged intermediate as in the toluene reaction discussed above. This has the merit of bringing the two antimony atoms close together. Methanolysis of the remaining chlorine atoms and nucleophilic attack of oxalate oxygens on antimony would then lead to the observed product.

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