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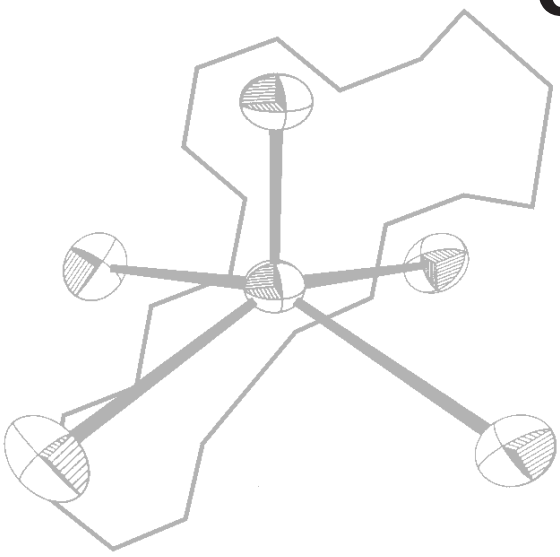

Volume 50, 1997

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Aust. J. Chem., 1997, **50**, 675–681

Structural Characterization of Some Novel Oxidation Products of Triphenylstibine

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Room-temperature single-crystal X-ray structural characterizations of two oxidation products of triphenylstibine of the form $XPh_3SbOSbPh_3X$ are recorded for X = Cl, NO_3. $ClPh_3SbOSbPh_3Cl$ is monoclinic, $P2_1/c$, $Z = 4$ f.u., a 9·109(4), b 19·809(8), c 19·30(2) Å, β 109·27(5)°, conventional R on $|F|$ being 0·038 for N_o 4431 'observed' ($I > 3\sigma(I)$) independent reflections. In this complex, Sb–O–Sb is quasi-linear, 173·1(3)°, in contrast to the previously recorded benzene solvate, in which it is 139·0(3)°; in the nitrate, $[(O_2NO)Ph_3SbOSbPh_3(ONO_2)]$, triclinic, $P\bar{1}$, $Z = 2$ f.u., a 15·609(5), b 13·238(4), c 10·140(2) Å, α 87·11(2), β 88·46(7), γ 72·93(2)°, R 0·036 for N_o 5275, it is also bent (137·0(2)°). The anionic substituent is opposed to the oxo bridge in the trigonal bipyramidal five-coordinate array about the metal in both complexes. A redetermination of the structure of $Ph_8Sb_4O_6$ is recorded, presenting a non-disordered model in a triclinic $P\bar{1}$ cell, a 19·698(3), b 11·635(2), c 9·739(2) Å, α 92·28(1), β 98·98(1), γ 99·74(1)°, $Z = 2$ f.u., R 0·046 for N_o 3578. A new ('β') phase of triphenylstibine, crystallized from hexane/toluene is also recorded: monoclinic, $P2_1/c$, a 15·386(8), b 11·304(5), c 19·078(8) Å, β 111·64(4)°, $Z = 8$, R 0·045 for N_o 3393.

Introduction

In accompanying papers[1–3] we describe syntheses and structural characterizations of adducts of triphenylstibine, Ph_3Sb (= L), with coinage metal(I) salts, MX, of formulation L_nMX for high n ($n = 3$, 4) and in which X may ($n < 4$) or may not ($n = 4$) be coordinated to the metal atom, the adducts having normally been successfully obtained by recrystallization from an appropriate supporting solvent (e.g. acetonitrile, pyridine). In the course of a number of these attempts, usually after abnormally extended standing at room temperature, small deposits of materials other than the desired products (and differing from the starting materials) have sometimes been obtained, these being characterized by room-temperature single-crystal X-ray studies with substantial certainty, given their history, as oxidation products of triphenylstibine, of the form $X(Ph_3Sb)O(SbPh_3)X$, in particular for X = Cl, NO_3, with the antimony pentavalent. As these studies fall outside the main thrust of our study we have not further pursued the mode of formation (oxidation by the metal, air, anion, etc.); nevertheless, the compounds are of sufficient novelty and interest to justify recording at the present effectively definitive level of characterization and we report this work hereunder. The compounds in question are (1) $OSb_2Ph_6Cl_2$, obtained from silver(I) chloride/triphenylstibine in 1 : 3 ratio in acetonitrile solution, and (2) $OSb_2Ph_6(NO_3)_2$, obtained from copper(I) nitrate/triphenylstibine in 1 : 3 ratio in toluene solution, as the toluene monosolvate.

The chloride is of particular interest; it has been the subject of a previous determination as a benzene disolvate.[4] The two determinations record radically different results in respect of the linearity or otherwise at the central oxygen. Curiously, a contemporary record of determinations of two different phases of the iodide has also been reported,[5] displaying a similar discrepancy and offering a basis for comparison.

We also take the opportunity to record a redetermination of tetranuclear $Ph_8Sb_4O_6$, deposited from a copper(I) perchlorate/triphenylstibine reaction mixture in 1 : 4 ratio in acetonitrile solution. We think there is good reason to believe the present form of the compound to be the same as that for which a structure determination has been previously recorded in a cell of half the size[6] with a totally disordered refinement model; the present model in the present

Manuscript received 7 March 1996 10.1071/CH96042 0004-9425/97/060675$05.00

Table 1. Non-hydrogen positional and isotropic displacement parameters for (1)

Atom	x	y	z	U_{eq}/Å^2
Sb(1)	0·59893(4)	0·49864(2)	0·18024(2)	0·0454(1)
Sb(2)	0·84530(5)	0·63291(2)	0·31853(2)	0·0487(2)
O	0·7174(4)	0·5641(2)	0·2541(2)	0·059(2)
Cl(1)	0·4409(2)	0·41832(8)	0·08123(9)	0·0670(7)
Cl(2)	1·0145(2)	0·71362(9)	0·4151(1)	0·0830(8)
C(111)	0·7862(6)	0·4798(3)	0·1417(3)	0·050(2)
C(112)	0·8590(8)	0·4183(3)	0·1572(4)	0·067(3)
C(113)	0·9922(8)	0·4070(4)	0·1387(4)	0·084(4)
C(114)	1·0474(8)	0·4558(5)	0·1048(4)	0·082(4)
C(115)	0·9728(9)	0·5161(4)	0·0891(4)	0·079(3)
C(116)	0·8415(8)	0·5298(3)	0·1070(3)	0·066(3)
C(121)	0·4243(6)	0·5708(3)	0·1354(3)	0·052(2)
C(122)	0·3775(8)	0·5881(3)	0·0625(3)	0·066(3)
C(123)	0·2779(9)	0·6410(4)	0·0380(4)	0·077(3)
C(124)	0·2182(9)	0·6745(4)	0·0831(5)	0·089(4)
C(125)	0·2621(9)	0·6571(4)	0·1559(5)	0·094(4)
C(126)	0·3655(8)	0·6055(4)	0·1825(3)	0·073(3)
C(131)	0·5852(7)	0·4293(3)	0·2611(3)	0·052(2)
C(132)	0·4548(8)	0·3894(4)	0·2504(4)	0·075(3)
C(133)	0·450(1)	0·3454(4)	0·3040(5)	0·094(4)
C(134)	0·573(1)	0·3386(4)	0·3672(5)	0·090(4)
C(135)	0·702(1)	0·3777(4)	0·3780(4)	0·087(4)
C(136)	0·7073(8)	0·4236(3)	0·3242(4)	0·070(3)
C(211)	0·6693(6)	0·6544(3)	0·3641(3)	0·049(2)
C(212)	0·6324(8)	0·7194(3)	0·3748(4)	0·077(3)
C(213)	0·5107(9)	0·7334(4)	0·3994(5)	0·095(4)
C(214)	0·4278(9)	0·6823(5)	0·4147(5)	0·090(4)
C(215)	0·4632(9)	0·6164(4)	0·4049(4)	0·082(4)
C(216)	0·5840(7)	0·6023(3)	0·3783(3)	0·061(3)
C(221)	0·8625(8)	0·6967(3)	0·2335(4)	0·060(3)
C(222)	0·9835(9)	0·7395(4)	0·2431(5)	0·086(4)
C(223)	0·987(1)	0·7782(4)	0·1826(6)	0·107(5)
C(224)	0·877(1)	0·7735(5)	0·1162(6)	0·112(6)
C(225)	0·756(1)	0·7299(5)	0·1065(5)	0·105(5)
C(226)	0·747(1)	0·6914(3)	0·1661(4)	0·082(4)
C(231)	1·0227(7)	0·5606(3)	0·3606(3)	0·055(2)
C(232)	1·0784(8)	0·5464(4)	0·4337(4)	0·081(3)
C(233)	1·184(1)	0·4943(5)	0·4579(5)	0·107(5)
C(234)	1·236(1)	0·4597(4)	0·4108(7)	0·107(5)
C(235)	1·1806(9)	0·4755(4)	0·3378(5)	0·097(4)
C(236)	1·0741(8)	0·5261(4)	0·3127(4)	0·076(3)

Table 2. Non-hydrogen positional and isotropic displacement parameters for (2)

Atom	x	y	z	U/Å^2
Sb(1)	0·77166(2)	0·98189(3)	0·79954(3)	0·0409(1)
Sb(2)	0·81133(2)	0·72623(3)	0·98126(3)	0·0427(1)
O	0·7721(2)	0·8813(3)	0·9489(3)	0·049(1)
O(11)	0·7738(2)	1·0942(3)	0·6219(3)	0·054(2)
O(12)	0·6306(3)	1·1704(3)	0·6415(4)	0·070(2)
O(13)	0·6963(3)	1·1710(5)	0·4527(5)	0·107(3)
N(1)	0·6970(3)	1·1481(4)	0·5704(5)	0·060(2)
O(21)	0·8515(2)	0·5496(3)	1·0175(4)	0·055(2)
O(22)	0·8448(3)	0·4177(4)	1·1475(5)	0·091(2)
O(23)	0·8200(3)	0·5725(4)	1·2277(4)	0·077(2)
N(2)	0·8379(3)	0·5119(4)	1·1363(6)	0·061(2)
C(111)	0·7341(3)	1·1116(4)	0·9230(5)	0·042(2)
C(112)	0·6937(4)	1·1028(5)	1·0442(6)	0·056(2)
C(113)	0·6748(4)	1·1843(6)	1·1280(6)	0·070(3)
C(114)	0·6974(4)	1·2747(5)	1·0933(7)	0·070(3)
C(115)	0·7377(5)	1·2845(5)	0·9738(7)	0·073(3)
C(116)	0·7563(4)	1·2023(5)	0·8888(6)	0·059(2)
C(121)	0·9099(3)	0·9351(4)	0·7595(5)	0·043(2)
C(122)	0·9658(4)	0·9156(5)	0·8653(6)	0·059(2)
C(123)	1·0583(4)	0·8803(6)	0·8471(7)	0·071(3)
C(124)	1·0932(4)	0·8637(5)	0·7224(7)	0·068(3)
C(125)	1·0383(4)	0·8823(5)	0·6158(6)	0·068(3)
C(126)	0·9464(4)	0·9180(5)	0·6337(6)	0·057(2)
C(131)	0·6803(4)	0·9332(5)	0·6902(6)	0·059(3)
C(132)	0·6918(5)	0·9162(6)	0·5559(7)	0·088(4)
C(133)	0·6304(8)	0·8809(8)	0·490(1)	0·129(6)
C(134)	0·5579(9)	0·8664(9)	0·555(1)	0·144(7)
C(135)	0·5447(6)	0·8820(8)	0·688(1)	0·123(5)
C(136)	0·6066(5)	0·9151(5)	0·7576(8)	0·082(3)
C(211)	0·8528(4)	0·6794(4)	0·7902(5)	0·047(2)
C(212)	0·7930(4)	0·6655(5)	0·7007(6)	0·066(3)
C(213)	0·8196(5)	0·6377(6)	0·5734(6)	0·076(3)
C(214)	0·9071(6)	0·6211(6)	0·5377(7)	0·080(3)
C(215)	0·9691(4)	0·6329(5)	0·6249(7)	0·072(3)
C(216)	0·9417(4)	0·6618(5)	0·7526(6)	0·058(2)
C(221)	0·6820(3)	0·7231(4)	1·0386(5)	0·047(2)
C(222)	0·6282(4)	0·8036(5)	1·1112(6)	0·063(3)
C(223)	0·5434(4)	0·8030(6)	1·1520(7)	0·077(3)
C(224)	0·5111(4)	0·7216(6)	1·1211(7)	0·073(3)
C(225)	0·5636(5)	0·6425(6)	1·0463(7)	0·081(3)
C(226)	0·6492(4)	0·6423(5)	1·0074(6)	0·063(3)
C(231)	0·9111(3)	0·7321(4)	1·1124(5)	0·045(2)
C(232)	0·9885(4)	0·6488(5)	1·1279(6)	0·056(2)
C(233)	1·0533(4)	0·6562(6)	1·2135(7)	0·071(3)
C(234)	1·0430(4)	0·7445(6)	0·2839(6)	0·074(3)
C(235)	0·9665(5)	0·8279(5)	1·2678(6)	0·070(3)
C(236)	0·9002(4)	0·8234(5)	1·1819(6)	0·057(2)
C(11)	0·5071(9)	0·604(1)	0·675(2)	0·20(1)
C(1)	0·5687(6)	0·5590(8)	0·609(1)	0·19(1)
C(2)	0·5814(7)	0·5852(6)	0·476(1)	0·148(8)
C(3)	0·6557(9)	0·5247(9)	0·4057(7)	0·20(1)
C(4)	0·7173(6)	0·4380(8)	0·469(1)	0·24(1)
C(5)	0·7045(7)	0·4119(6)	0·602(1)	0·31(2)
C(6)	0·6303(9)	0·4723(9)	0·6718(7)	0·22(1)

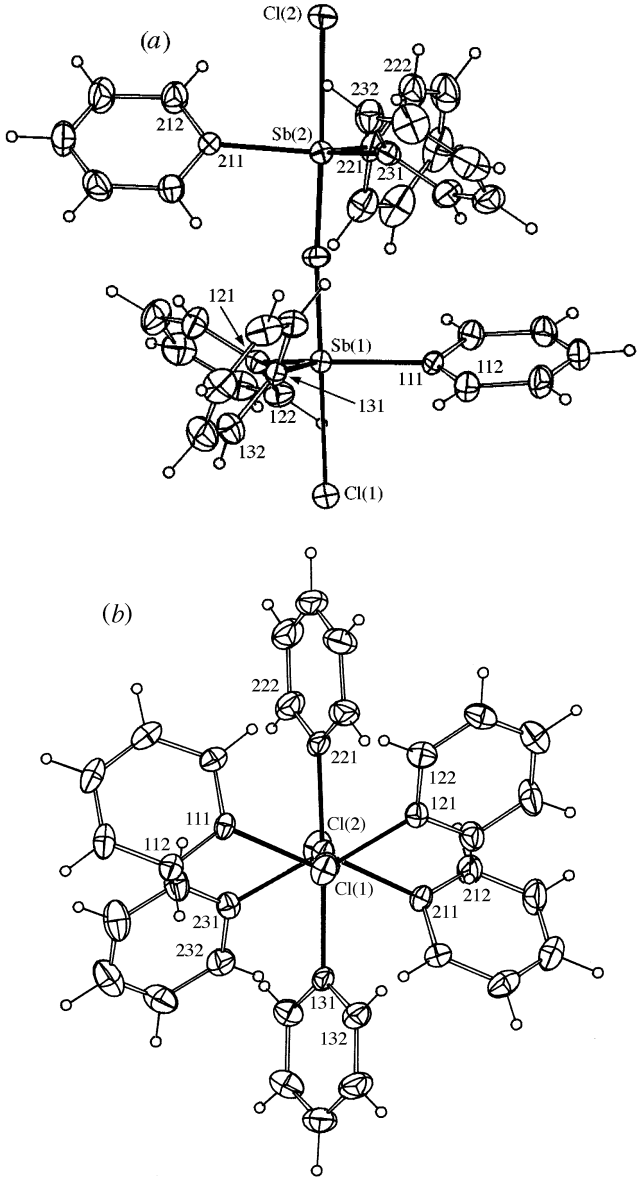
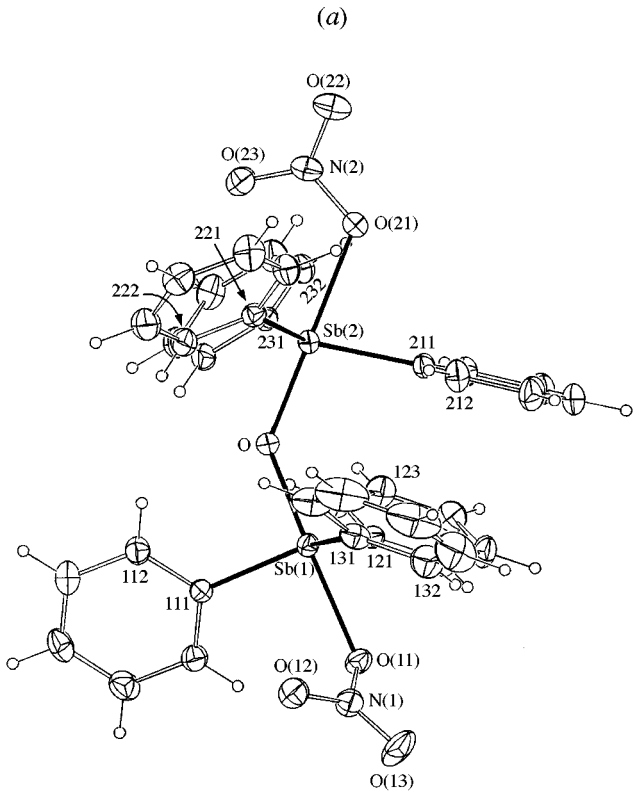


Fig. 1. Projection of $Cl(Ph_3Sb)O(SbPh_3)Cl$: (*a*) normal to; (*b*) down the Sb···Sb line.



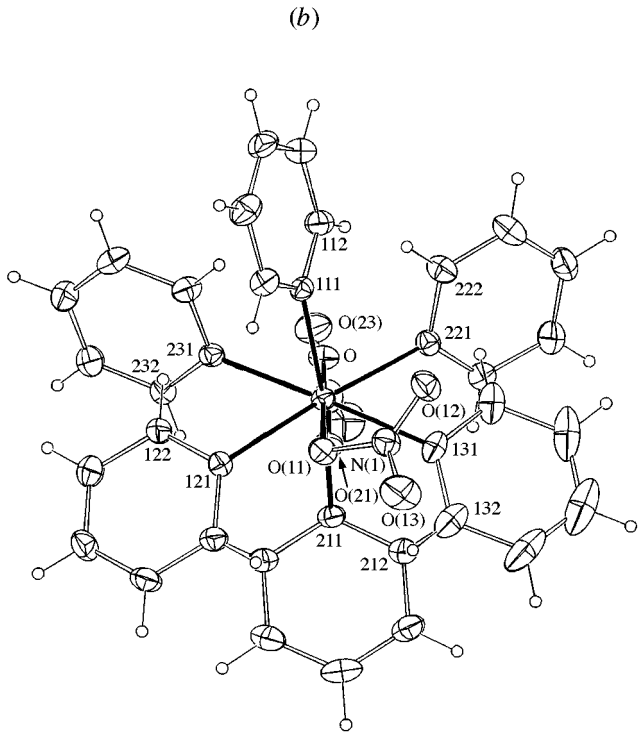
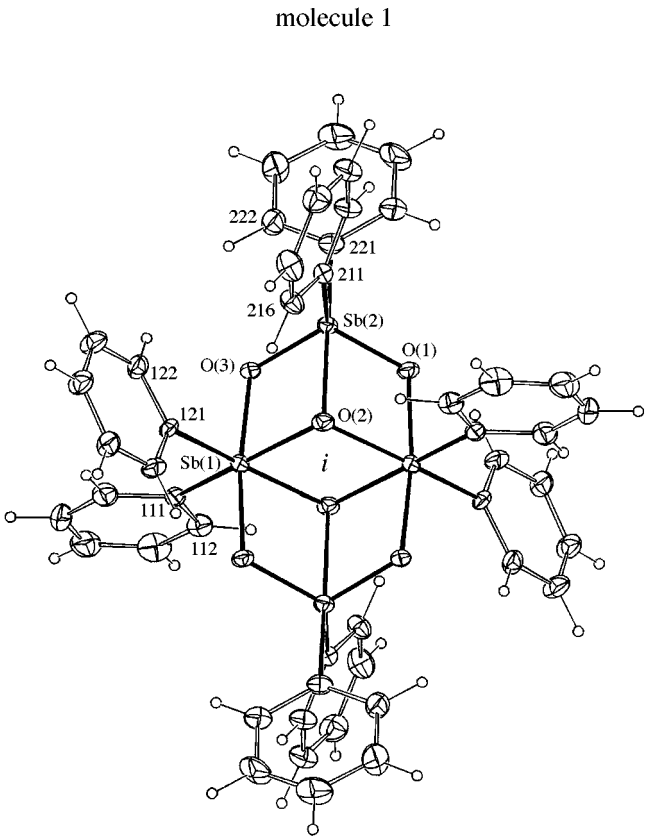


Fig. 2. Projections of $[(O_2NO)(Ph_3Sb)O(SbPh_3)(ONO_2)]$: (*a*) normal to; (*b*) down the Sb···Sb line.



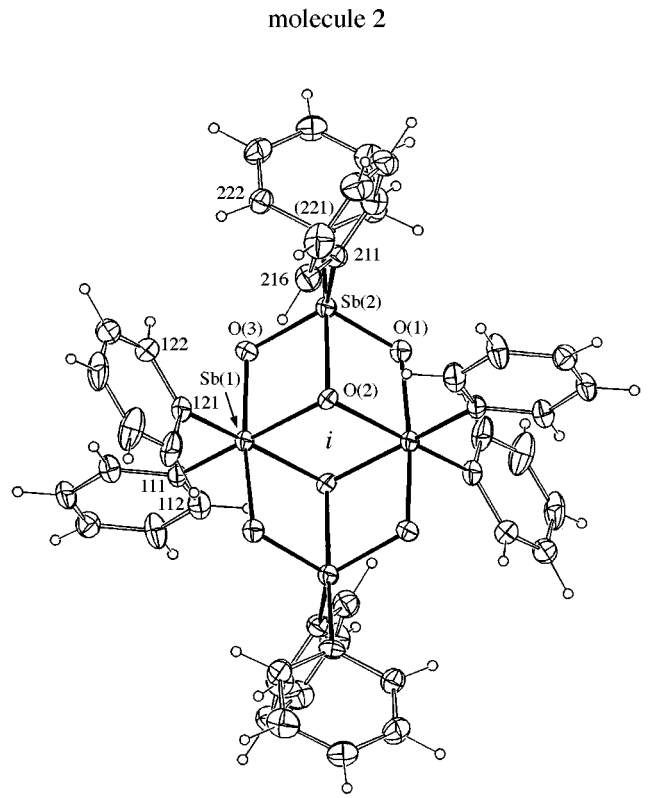


Fig. 3. The two molecules of $Ph_8Sb_4O_6$.

Table 3. Non-hydrogen positional and isotropic displacement parameters for (3)

Atom	x	y	z	U/Å^2
		Molecule 1		
Sb(1)	0·48015(5)	0·05847(8)	0·64534(9)	0·0344(4)
Sb(2)	0·54245(5)	−0·17868(8)	0·6437(1)	0·0380(4)
O(1)	0·5823(4)	−0·1454(7)	0·4820(9)	0·045(4)
O(2)	0·4609(4)	−0·0969(7)	0·5135(9)	0·040(4)
O(3)	0·5449(4)	−0·0370(7)	0·7493(8)	0·043(4)
C(111)	0·5309(8)	0·212(1)	0·771(1)	0·044(6)
C(112)	0·5888(7)	0·285(1)	0·741(2)	0·050(6)
C(113)	0·6178(9)	0·385(1)	0·826(2)	0·073(8)
C(114)	0·590(1)	0·417(2)	0·936(2)	0·09(1)
C(115)	0·533(1)	0·346(2)	0·964(2)	0·074(9)
C(116)	0·5027(8)	0·245(1)	0·883(2)	0·059(7)
C(121)	0·3959(7)	−0·008(1)	0·749(1)	0·035(5)
C(122)	0·4043(8)	−0·069(1)	0·864(1)	0·051(6)
C(123)	0·3494(9)	−0·116(1)	0·929(2)	0·061(7)
C(124)	0·2827(8)	−0·103(1)	0·873(2)	0·060(7)
C(125)	0·2729(8)	−0·040(1)	0·763(2)	0·057(7)
C(126)	0·3290(8)	0·006(1)	0·698(1)	0·051(6)
C(211)	0·4647(8)	−0·324(1)	0·643(1)	0·044(6)
C(212)	0·4835(8)	−0·430(1)	0·664(2)	0·057(7)
C(213)	0·434(1)	−0·531(1)	0·663(2)	0·071(8)
C(214)	0·364(1)	−0·523(1)	0·647(2)	0·073(8)
C(215)	0·3434(8)	−0·415(2)	0·628(2)	0·072(8)
C(216)	0·3934(8)	−0·316(1)	0·628(2)	0·051(6)
C(221)	0·6301(7)	−0·229(1)	0·764(2)	0·048(6)
C(222)	0·6500(8)	−0·193(1)	0·903(2)	0·065(8)
C(223)	0·707(1)	−0·227(2)	0·983(2)	0·09(1)
C(224)	0·7438(9)	−0·297(2)	0·922(2)	0·09(1)
C(225)	0·727(1)	−0·333(2)	0·784(2)	0·09(1)
C(226)	0·6702(9)	−0·301(1)	0·706(2)	0·067(8)
		Molecule 2		
Sb(1)	−0·06531(5)	0·54540(8)	0·3960(1)	0·0475(4)
Sb(2)	−0·08348(5)	0·28823(9)	0·5052(1)	0·0483(4)
O(1)	−0·0087(5)	0·3300(8)	0·656(1)	0·054(4)
O(2)	−0·0073(4)	0·4126(7)	0·4115(9)	0·050(4)
O(3)	−0·1301(5)	0·4154(8)	0·462(1)	0·060(4)
C(111)	−0·1259(7)	0·670(1)	0·458(2)	0·049(6)
C(112)	−0·1107(9)	0·727(2)	0·586(2)	0·072(8)
C(113)	−0·147(1)	0·812(2)	0·622(2)	0·080(9)
C(114)	−0·2011(9)	0·837(1)	0·525(2)	0·065(8)
C(115)	−0·2168(9)	0·780(1)	0·401(2)	0·074(8)
C(116)	−0·1802(9)	0·693(1)	0·361(2)	0·071(8)
C(121)	−0·1070(8)	0·500(1)	0·182(2)	0·060(7)
C(122)	−0·1705(9)	0·425(1)	0·141(2)	0·071(8)
C(123)	−0·193(1)	0·394(2)	−0·004(3)	0·09(1)
C(124)	−0·159(1)	0·445(2)	−0·104(2)	0·09(1)
C(125)	−0·099(1)	0·518(2)	−0·061(2)	0·11(1)
C(126)	−0·0734(9)	0·548(2)	0·078(2)	0·09(1)
C(211)	−0·0739(8)	0·164(1)	0·350(2)	0·058(7)
C(212)	−0·0748(9)	0·052(2)	0·388(2)	0·071(8)
C(213)	−0·067(1)	−0·037(2)	0·289(3)	0·09(1)
C(214)	−0·056(1)	−0·005(2)	0·162(2)	0·09(1)
C(215)	−0·055(1)	0·104(2)	0·125(2)	0·09(1)
C(216)	−0·0629(9)	0·192(2)	0·217(2)	0·073(8)
C(221)	−0·1548(8)	0·197(1)	0·617(2)	0·050(6)
C(222)	−0·2276(8)	0·187(1)	0·570(2)	0·063(7)
C(223)	−0·2741(9)	0·126(2)	0·637(2)	0·074(8)
C(224)	−0·256(1)	0·071(2)	0·756(2)	0·071(8)
C(225)	−0·185(1)	0·080(2)	0·802(2)	0·08(1)
C(226)	−0·1367(8)	0·142(1)	0·733(2)	0·066(7)

Table 4. Non-hydrogen positional and isotropic displacement parameters for (4)

Atom	x	y	z	U_{eq}/Å^2
Sb(1)	0·47337(4)	0·30358(4)	0·58651(3)	0·0835(3)
Sb(2)	0·16069(4)	0·44661(5)	0·39522(3)	0·0776(2)
C(111)	0·4178(5)	0·2727(6)	0·4671(3)	0·068(3)
C(112)	0·3701(5)	0·1704(6)	0·4347(4)	0·078(3)
C(113)	0·3372(5)	0·1558(7)	0·3571(4)	0·084(4)
C(114)	0·3487(5)	0·2421(7)	0·3119(4)	0·088(4)
C(115)	0·3947(5)	0·3444(8)	0·3417(4)	0·094(4)
C(116)	0·4271(5)	0·3598(6)	0·4190(4)	0·086(4)
C(121)	0·4173(5)	0·1464(6)	0·6165(3)	0·066(3)
C(122)	0·4663(5)	0·0424(6)	0·6372(4)	0·080(3)
C(123)	0·4275(5)	−0·0573(7)	0·6545(4)	0·098(4)
C(124)	0·3368(6)	−0·0513(8)	0·6518(4)	0·102(4)
C(125)	0·2874(5)	0·0508(8)	0·6323(5)	0·106(4)
C(126)	0·3270(5)	0·1497(7)	0·6146(4)	0·091(4)
C(131)	0·6098(5)	0·2359(6)	0·6046(4)	0·078(3)
C(132)	0·6313(5)	0·1650(7)	0·5539(4)	0·088(4)
C(133)	0·7199(6)	0·1279(7)	0·5662(4)	0·100(4)
C(134)	0·7910(6)	0·1603(9)	0·6305(5)	0·116(5)
C(135)	0·7750(6)	0·229(1)	0·6819(5)	0·134(5)
C(136)	0·6856(6)	0·2664(8)	0·6688(4)	0·109(4)
C(211)	0·0748(4)	0·3051(6)	0·4093(3)	0·067(3)
C(212)	−0·0191(5)	0·3159(6)	0·3920(4)	0·078(3)
C(213)	−0·0725(5)	0·2199(7)	0·3964(4)	0·095(4)
C(214)	−0·0300(6)	0·1118(7)	0·4165(4)	0·100(4)
C(215)	0·0644(6)	0·1000(7)	0·4362(4)	0·096(4)
C(216)	0·1168(5)	0·1940(7)	0·4319(4)	0·080(3)
C(221)	0·0537(5)	0·5800(6)	0·3640(4)	0·071(3)
C(222)	0·0414(5)	0·6590(6)	0·4144(4)	0·076(3)
C(223)	−0·0268(5)	0·7451(7)	0·3915(4)	0·087(4)
C(224)	−0·0824(6)	0·7546(8)	0·3168(5)	0·101(4)
C(225)	−0·0720(6)	0·6767(8)	0·2665(4)	0·108(4)
C(226)	−0·0048(5)	0·5902(7)	0·2891(4)	0·091(4)
C(231)	0·2213(4)	0·4949(6)	0·5117(4)	0·069(3)
C(232)	0·1912(5)	0·4557(7)	0·5663(4)	0·077(3)
C(233)	0·2323(5)	0·4895(7)	0·6407(4)	0·094(4)
C(234)	0·3075(6)	0·5660(8)	0·6610(4)	0·105(4)
C(235)	0·3393(5)	0·6075(8)	0·6070(5)	0·116(5)
C(236)	0·2973(5)	0·5739(7)	0·5327(5)	0·092(4)

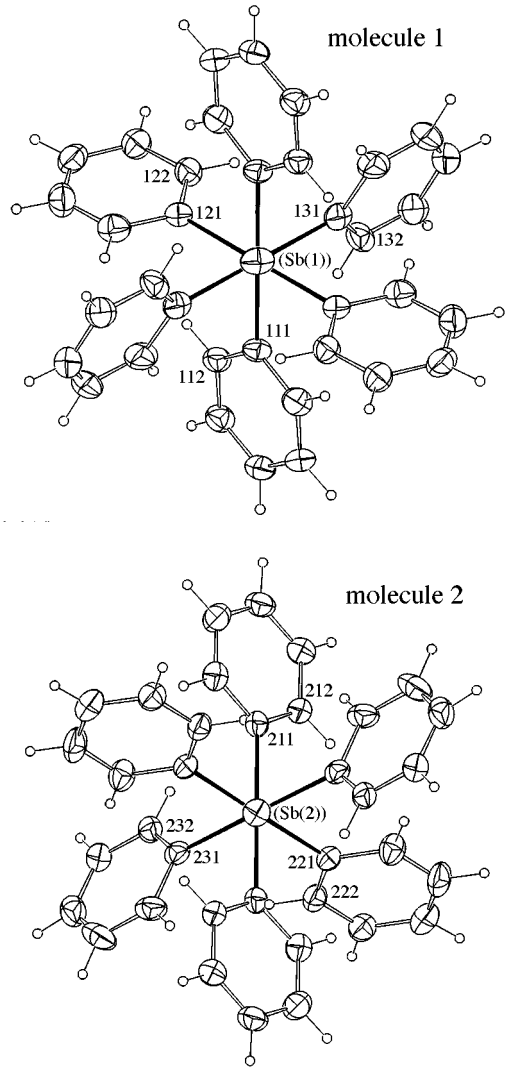


Fig. 4. The two molecules of the asymmetric unit of 'β'-triphenylstibine, projected pairwise with their inversion images down the Sb···Sb lines.

Table 5. Molecular core geometries for (1), (2) and related compounds $XPh_3SbOSbPh_3X$

Column headings Sb(1), Sb(2) identify Sb(n)

	(1) X = Cl[A]		X = Cl.C_6H_6[B]		X = Br (mol. 1)		X = Br (mol. 2)[C]		X = N_3[D]	(2) X = ONO_2[A,E]	
	Sb(1)	Sb(2)	Sb(1)	Sb(2)	Sb(1)	Sb(2)	Sb(1)	Sb(2)	Sb	Sb(1)	Sb(2)
					Distances/Å						
Sb–O	1·965(4)	1·951(4)	1·980(6)	1·986(6)	1·96(1)	1·93(1)	1·94(1)	1·94(1)	1·985(3)	1·965(3)	1·975(3)
Sb–O/X(n)	2·537(2)	2·551(2)	2·553(2)	2·582(3)	2·707(4)	2·722(3)	2·716(3)	2·693(3)	2·236(8)	2·283(4)	2·250(4)
Sb–C(n11)	2·106(6)	2·111(7)	2·130(9)	2·13(1)	2·09(2)	2·11(2)	2·09(2)	2·11(2)	2·112(9)	2·109(5)	2·091(5)
Sb–C(n21)	2·101(5)	2·117(7)	2·12(1)	2·116(8)	2·09(2)	2·08(2)	2·08(2)	2·06(2)	2·107(8)	2·097(5)	2·098(6)
Sb–C(n31)	2·114(6)	2·111(6)	2·118(8)	2·109(8)	2·07(2)	2·12(2)	2·14(2)	2·09(2)	2·128(7)	2·092(7)	2·096(5)
Sb···Sb	3·909(2)		3·714(1)		3·875(1)		3·884(1)		3·726(1)	3·665(1)	
					Angles/degrees						
Sb–O–Sb	173·1(3)		139·0(3)		170·2(7)		176·6(8)		139·8(4)	137·0(2)	
O–Sb–O/X(n)	177·6(1)	173·3(1)	177·0(2)	174·0(2)	178·8(4)	178·8(4)	178·6(4)	178·5(4)	178·3(3)	178·1(1)	178·2(1)
O–Sb–C(n11)	93·3(2)	91·8(2)	91·7(3)	90·3(3)	92·8(7)	90·3(6)	92·2(7)	90·6(6)	92·3(3)	91·9(2)	99·7(2)
O–Sb–C(n21)	90·6(2)	96·0(2)	92·3(3)	98·6(3)	90·2(7)	92·9(6)	91·8(7)	89·6(6)	95·1(3)	97·7(2)	92·5(2)
O–Sb–C(n31)	92·6(2)	89·5(2)	91·3(3)	88·6(3)	90·1(7)	89·2(6)	90·0(7)	90·7(6)	91·3(3)	94·3(2)	92·8(2)
O/X(n)–Sb–C(n11)	87·0(2)	85·9(2)	87·3(2)	87·9(3)	88·3(6)	88·9(5)	87·5(5)	90·7(5)	87·1(3)	89·9(2)	80·5(2)
O/X(n)–Sb–C(n21)	87·3(2)	90·6(2)	86·2(3)	87·3(3)	88·8(6)	88·3(5)	89·6(5)	89·0(5)	83·9(2)	81·1(2)	85·8(2)
O/X(n)–Sb–C(n31)	89·5(2)	86·7(2)	91·7(2)	87·6(3)	89·9(6)	90·4(5)	89·1(5)	89·6(5)	90·4(3)	85·1(2)	88·7(2)
C(n11)–Sb–C(n21)	124·5(2)	117·6(2)	128·0(3)	120·0(4)	124·4(8)	118·6(8)	119·8(8)	122·9(8)	125·6(3)	111·7(2)	116·3(2)
C(n11)–Sb–C(n31)	113·4(2)	124·5(2)	113·1(4)	122·5(3)	117·8(8)	121·4(8)	124·2(8)	117·4(8)	117·8(3)	123·5(2)	117·1(2)
C(n21)–Sb–C(n31)	121·6(3)	117·4(3)	118·6(4)	117·0(4)	117·7(8)	120·0(9)	115·9(8)	119·7(8)	115·8(3)	122·8(2)	124·5(2)
Σ C–Sb–C	359·5	359·5	359·7	359·5	359·9	360·0	359·9	360·0	359·2	358·0	357·9
					Torsion angles/degrees (the acute angle is given)						
O–Sb–C(n11)–C(n12/6)	−65·8(4)	39·7(4)	43·6(5)	26·6(5)	−47(1)	52(1)	−53(1)	46(1)	−33·5(5)	−20·9(4)	−86·7(5)
O–Sb–C(n21)–C(n22/6)	−49·6(5)	23·6(6)	−54·2(5)	−74·2(5)	−48(1)	64(1)	−52(1)	46(1)	50·7(5)	−42·7(5)	−37·5(5)
O–Sb–C(n31)–C(n32/6)	−35·7(6)	54·1(5)	−18·7(5)	−50·5(5)	−63(1)	45(1)	−46(1)	54(1)	17·2(5)	42·7(5)	26·9(5)

[A] This work. [B] Ref. 4. [C] Ref. 7. [D] Ref. 8. [E] Nitrate geometries (n = 1,2) in (2): N(n)–O(n1,2,3) 1·308(6), 1·317(7); 1·218(6), 1·220(8); 1·217(7), 1·229(7) Å; O(n1)–N(n)–O(n2) 118·7(5), 116·7(5); O(n1)–N(n)–O(n3) 117·4(5), 118·7(5); O(n2)–N(n)–O(n3) 123·9(5), 124·5(6); Sb(n)–O(n1)–N(n) 117·9(3), 118·1(3)°. Deviations of Sb(n) from the NO_3(n) planes: 0·998(9), 0·448(9) Å.

Table 6. Molecular non-hydrogen geometries in $Ph_8Sb_4O_6$: the antimony environments

Values[A] for molecule 2 follow those for molecule 1; primed atoms are inversion-related

Sb(1)	r	O(3)	O(1′)	O(2′)	C(111)	C(121)	Sb(2)	r	O(2)	O(3)	C(211)	C(221)
O(2)	2·119(8)	78·1(3)	95·9(3)	74·7(3)	162·8(5)	90·8(4)	O(1)	1·891(9)	77·5(4)	109·4(4)	120·6(5)	97·6(5)
	2·069(9)	77·5(4)	97·4(5)	74·6(3)	159·0(5)	93·7(5)		1·891(8)	77·8(4)	111·6(4)	118·1(5)	97·3(5)
O(3)	2·013(9)		172·7(4)	95·7(4)	91·1(5)	93·3(4)	O(2)	2·251(8)		77·3(3)	86·9(4)	170·6(4)
	2·001(9)		173·5(4)	97·5(4)	90·4(5)	93·5(5)		2·231(9)		75·7(4)	86·3(5)	169·9(5)
O(1′)	2·029(9)			78·5(4)	93·7(5)	91·0(4)	O(3)	1·897(8)			122·4(5)	97·1(5)
	2·012(9)			77·2(3)	93·3(5)	90·8(5)		1·898(10)			121·6(5)	98·4(5)
O(2′)	2·093(9)				93·3(5)	160·9(4)	C(211)	2·08(1)				102·5(5)
	2·156(8)				90·3(5)	161·7(5)		2·10(2)				103·8(6)
C(111)	2·13(1)					103·3(5)	C(221)	2·12(1)				
	2·15(2)					104·3(6)		2·09(2)				
C(121)	2·13(1)											
	2·13(2)											

[A] Other: Sb(1)···Sb(2,1′,2′) 3·205(2), 3·350(1), 3·194(1); 3·197(2), 3·361(2), 3·211(2) Å; Sb(1)–O(1)–Sb(2′) 109·1(5); 110·7(5); Sb(1)–O(3)–Sb(2) 110·1(4); 110·1(5); Sb(1)–O(2)–Sb(2,1′) 94·3(3), 105·3(3); 96·0(4), 105·4(4); Sb(2)–O(2)–Sb(1′) 94·6(3); 94·1(4)°.

Table 7. Pendant carbon angles and phenyl torsion angles in $Ph_8Sb_4O_6$

Feature	Atoms	Angles/degrees (mols 1; 2)
Pendant carbon angles	Sb(1)–C(111)–C(112,6)	123(1), 119(1); 122(1), 118(1)
	Sb(1)–C(121)–C(122,6)	123(1), 121(1); 121(1), 121(1)
	Sb(2)–C(211)–C(212,6)	119(1), 122(1); 117(1), 123(1)
	Sb(2)–C(221)–C(222,6)	121(1), 121(1); 120(1), 124(1)
Phenyl torsion angles	O(2)–Sb(1)–C(111)–C(112,6)	37(2), −148(1); 38(2), −144(1)
	O(2)–Sb(1)–C(121)–C(122,6)	91(1), −87(1); 93(1), −90(2)
	O(2)–Sb(2)–C(211)–C(212,6)	156(1), −27(1); 143(1), −33(1)
	O(2)–Sb(2)–C(221)–C(222,6)	79(3), −101(3); 94(3), −87(3)

cell is well behaved. Further, we record a new phase ('β') of triphenylstibine, obtained from hexane/toluene solution.

Structure Determination

General procedures are given in ref. 1; specific details are as follows (see also Tables 1–7 and Figs 1–4).

(1) [(Cl)Ph$_3$SbOSbPh$_3$(Cl)]. $C_{36}H_{30}Cl_2OSb_2$, M 793·0. Monoclinic, space group $P2_1/c$ (C_{2h}^5, No. 14), a 9·109(4), b 19·809(8), c 19·30(2) Å, β 109·27(5)°, V 3287 Å^3. D_c(Z = 4 f.u.) 1·60 g cm^{-3}; F(000) 1560. μ_{Mo} 16·9 cm^{-1}; specimen: 0·46 by 0·40 by 0·39 mm; $A^*_{min,max}$ 1·66, 1·81. $2\theta_{max}$ 50°; N 5757, N_o 4431; R 0·038, R_w 0·044.

(2) [(O$_2$NO)Ph$_3$SbOSbPh$_3$(ONO$_2$)].C$_7$H$_8$. $C_{43}H_{38}N_2O_7Sb_2$, M 937·9. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a 15·609(5), b 13·238(4), c 10·140(2) Å, α 87·11(2), β 88·46(7), γ 72·93(2)°, V 2001 Å^3. D_c(Z = 2 f.u.) 1·56 g cm^{-3}; F(000) 936. μ_{Mo} 14·0 cm^{-1}; specimen: 0·32 by 0·14 by 1·00 mm; $A^*_{min,max}$ 1·20, 1·60. $2\theta_{max}$ 50°; N 7026, N_o 5275; R 0·036, R_w 0·039.

Variata for (2). The toluene molecule, although exhibiting high thermal motion, refined to unit population and with no overt disorder; in final refinement cycles it was modelled as a rigid body.

(3) Ph$_8$Sb$_4$O$_6$. $C_{48}H_{40}O_6Sb_4$, M 1199·5. Triclinic, space group $P\bar{1}$, a 19·698(3), b 11·635(2), c 9·739(2) Å, α 92·28(1), β 98·98(1), γ 99·74(1)°, V 2168 Å^3. D_c(Z = 2 f.u.) 1·84 g cm^{-3}; F(000) 1160. μ_{Mo} 25·4 cm^{-1}; specimen: 0·10 by 0·24 by 0·18 mm; $A^*_{min,max}$ 1·15, 1·63. $2\theta_{max}$ 45°; N 5295, N_o 3578; R 0·046, R_w 0·047.

(4) Ph$_3$Sb. $C_{18}H_{15}Sb$, M 353·1. Monoclinic, space group $P2_1/c$, a 15·386(8), b 11·304(5), c 19·078(8) Å, β 111·64(4)°, V 3084 Å^3. D_c(Z = 8) 1·52 g cm^{-3}; F(000) 1392. μ_{Mo} 17·7 cm^{-1}; specimen: 0·55 by 0·20 by 0·35 mm; $A^*_{min,max}$ 1·41, 1·84. $2\theta_{max}$ 50°; N 5427, N_o 3393; R 0·045, R_w 0·046.

Discussion

Given the histories of the materials, the results of the room-temperature single-crystal X-ray studies of the first two complexes are consistent in likely stoichiometry and connectivity with their formulation as members of the well known family of oxo-bridged antimony(V) compounds X(Ph$_3$Sb)O(SbPh$_3$)X, two five-coordinate antimony(V) species being bridged by an oxygen atom lying axially *trans* in a quasi-trigonal bipyramidal coordination sphere to a unidentate anion, the three phenyl groups being equatorial; the anions are chloride and *O*-nitrate respectively, the latter complex being produced as a toluene solvate. A considerable variety of related compounds has been structurally characterized; those considered most relevant, comprising compounds of the type XPh$_3$SbOSbPh$_3$X, X = halide or pseudo-halide, viz. Cl (as benzene solvate),[4] Br,[7] N$_3$,[8] are summarized geometrically in company with the present in Table 5. Also worthy of passing note is the very recent structural record of binuclear homologues [XPh$_2$Sb(μ-O)$_{2/2}$]$_2$.[9] Geometries of the present two systems are given in detail in Table 5; the molecules are depicted in Figs 1 and 2. Features initially worthy of note are the 'staggered' disposition of the phenyl groups in projection down the Sb···Sb line, the substantial differences in the Sb–O–Sb angles, and the unidentate coordination of the nitrate groups in that complex, involving unusually lengthened N–O distances.

Of particular note is the characterization of a second phase of the chloride and the observation of a remarkable difference in the angles subtended at the central oxygen atom by the two antimony atoms, these being 139·0(3)° in the previously studied benzene solvate[4] and 173·1(3)° in the present. By a remarkable coincidence, the results of an equally remarkable contemporary study have just appeared, recording the structural characterization of two polymorphs of the iodide analogue,[5] neither being isomorphous with the present chloride. The two iodide polymorphs display angles of 180° and 144·6(4)° at the central oxygen, the variation in angle correlating with variations in Sb–O (1·9410(6), 1·9437(6) versus 1·986(8), 1·956(8) Å) and Sb–I (2·954(1), 2·968(1) versus 2·991(3), 2·995(1) Å); counterpart values in the chloride systems for Sb–O are 1·965(4), 1·951(4) versus 1·980(6), 1·986(6) Å, supporting a similar correlation with change in angle. In both sets of examples, the angular values of linearity and *c.* 140° correspond to the dichotomy defined for such compounds by Glidewell.[10]

The structural characterization of 'Ph$_8$Sb$_4$O$_6$' resides in the literature in two forms; one, recorded as [(Ph$_8$Sb$_4$O$_6$).(HOAc)$_3$] dichloromethane solvate,[11] is a true tetranuclear basic acetate and, as such, not strictly comparable with the 'unsolvated' bare parent. The latter has been recorded in a triclinic cell; a 11·677(5), b 9·745(3), c 10·586(6) Å, α 99·69(4), β 113·35(3), γ 87·56(3)°, V 1090 Å^3, Z = 1 f.u.; the structure was refined to a residual of 0·051 for 2175 'observed' ($I > 3\sigma(I)$) reflections in terms of a model involving a pair of essentially identical tetranuclear molecules superimposed and centred about a common inversion centre and disordered 50 : 50 in that manner.[6] The

close similarity of a and b, $180-\gamma$, and V of that determination with the present b, c, α and $V/2$ suggested the present cell and refinement in terms of a non-disordered model comprising a pair of independent centrosymmetric tetranuclear molecules, one-half of each constituting the asymmetric unit, to be a more appropriate description of an essentially similar structure, notwithstanding the very acceptable residual in the refinement of the earlier disordered model. The present resulting pair of molecules and their associated very similar geometries are presented in Fig. 3 and Tables 6 and 7, the most obvious non-trivial differences being in respect of the disposition of the pendant phenyl rings about the periphery. The novel array of the Sb_4O_6 core comprises a pair of open cubes, each with one corner missing with a common face containing an inversion centre which relates them, the overall symmetry being quasi-$2/m$.

A new crystalline ('β') phase of the parent triphenylstibine has been obtained from toluene/hexane solution. As in the other (triclinic) phase,[12] there are two molecules in the asymmetric unit; these are packed so as to confront each other, with lone pairs everted, presumably in consequence of intermolecular interactions of a type recently described.[13] Geometries are unexceptional with Sb–C ranging from $2\cdot140(7)$ to $2\cdot155(7)$ Å (average $2\cdot14_6$ Å) and torsions C($mn1$)–Sb(m)–C(mn+1 1)–C(mn+1 2) $93\cdot3(6)$, $94\cdot8(6)$, $79\cdot9(6)$; $102\cdot8(6)$, $95\cdot8(6)$, $85\cdot7(6)°$, $n = 1$, 2, 3 respectively for molecules $m = 1$, 2.

Acknowledgment

We gratefully acknowledge correspondence with Professor Michael J. Taylor of the Department of Chemistry, University of Auckland,[14] recording the synthesis of the above phase of $(Ph_3SbCl)_2O$ (confirmed by a unit cell calibration) following the method recorded in ref. 7 for the bromide. He reports the presence of a (slightly split) band at 765 cm^{-1}, attributed to Sb–O, similar to that recorded for the product reported in ref. 15.

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