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Oxidation of tetraaryldistibanes: syntheses and crystal structures of diarylantimony oxides and peroxides, $(R_2Sb)_2O$, $(R_2Sb)_4O_6$ and $(R_2SbO)_4(O_2)_2$ (R = Ph, *o*-Tol, *p*-Tol)

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Abstract

Tetraaryldistibanes, $(R_2Sb)_2$ (R = Ph, *o*-Tol, *p*-Tol) are synthesized by the reactions of R_2SbNa with $BrCH_2CH_2Br$ in liquid ammonia. They react with air oxygen to form $(R_2Sb)_2O$ and $(R_2Sb)_4O_6$. The reactions of $(R_2Sb)_4O_6$ with H_2O_2 give peroxides, $(R_2SbO)_4(O_2)_2$. Single-crystal X-ray structure analyses reveal that the conformations of the $(R_2Sb)_2O$ molecules are close to *syn–syn* (R = Ph) or to *syn–anti* (R = *o*-Tol, *p*-Tol). $(Ph_2SbO)_4(O_2)_2$ is an antimony-oxygen cluster with μ_4-peroxo ligands.

Keywords: Antimony; Oxygen; Peroxides; X-ray diffraction

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1. Introduction

Tetraorganodistibanes, $(R_2Sb)_2$, (R = alkyl, aryl [1]) are extremely air sensitive compounds. Many alkyl derivatives ignite spontaneously when exposed to air. Tetraaryldistibanes are less reactive, but in solution they also readily absorb oxygen from the atmosphere. Reactions of distibanes with air have been studied since the 1920s and the formation of a stibinic acid $R_2Sb(O)OH$ (R = Me) [2] and a peroxide $R_2SbOOSbR_2$ (R = Ph) [3] were reported in the earlier literature. Later we used infrared and mass spectroscopy to show that the air oxidation of tetraalkyldistibanes leads to monoxides $(R_2Sb)_2O$ (R = Me, Et, *i*-Pr) [4] in the first step. It is, however, difficult to stop the oxidation of the alkyl derivatives at this stage and the products formed by complete oxidation are ill defined [2,4]. The expectation that under protection of aryl groups the stepwise oxidation might be feasible prompted our study of reactions of representative tetraaryldistibanes, $(R_2Sb)_2$ (R = Ph, *o*-Tol, *p*-Tol) with air and H_2O_2 and we report here the syntheses of monoxides, $(R_2Sb)_2O$, hexoxides, $(R_2Sb)_4O_6$, and peroxo clusters, $(R_2SbO)_4(O_2)_2$. A part of the results was already reported in a short communication [5]. $(R_2Sb)_2O$ (R = Ph [1], *p*-Tol [1]), and $(R_2Sb)_4O_6$ (R = Ph [6], *o*-Tol [7]) are known compounds, which were prepared before by other methods.

2. Results and discussion

2.1. Synthesis and oxidation of $(R_2Sb)_2$ and crystal structures of $(R_2Sb)_2O$ (R = Ph, o-Tol, p-Tol)

The tetraaryldistibanes, $(R_2Sb)_2$ (R = Ph [8], *o*-Tol, *p*-Tol) were prepared as yellow solids by reactions of R_2SbNa with $BrCH_2CH_2Br$ and crystallization from diethylether. This method, which is well known for the synthesis of the phenyl derivative, is equally useful for the preparation of the tolyl compounds, although the yields are low. $(o\text{-}Tol_2Sb)_2$ is a novel distibane, whereas $(p\text{-}Tol_2Sb)_2$ is known for a long time as a product of the reduction of R_2SbI with sodium hypophosphite [9].

The monoxides $(R_2Sb)_2O$ (R = Ph, *o*-Tol, *p*-Tol) form in quantitative yields, when solutions of the distibanes in diethyl ether are exposed to the air under conditions that allow very slow absorption of oxygen. This process is easily achieved by repeatedly opening

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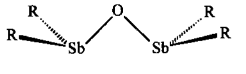
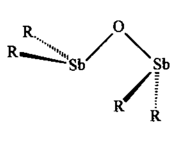
and closing the stopper of the reaction flasks until the yellow solutions discolour.

$$(R_2Sb)_2 + 1/2\,O_2 \rightarrow (R_2Sb)_2O \quad R = Ph, o\text{-Tol}, p\text{-Tol} \tag{1}$$

Advantages of the oxidation (1) compared with hydrolyses of diarylantimony halides [1] are simple work-up procedures and high yields.

Interesting aspects of the structures of the $(R_2Sb)_2O$ molecules are the conformational preferences, which are described by the Ep–Sb–O–Sb torsional angles φ. Ep stands for the assumed direction of the lone pair at the antimony atoms. With assignment of the terms *syn* and *anti* for angles of 0 and 180°, the extreme conformations are *syn–syn* and *syn–anti* [10,11].





The molecular structures of $(R_2Sb)_2O$ (R = Ph, *o*-Tol, *p*-Tol) were determined by X-ray crystallography on single crystals obtained from diethyl ether or toluene. They are depicted in Fig. 1. Crystallographic data are presented in Table 1. Despite the close relations between these molecules their conformations are not uniform. The structure of $(Ph_2Sb)_2O$ consists of molecules in a conformation close to *syn–syn* ($\varphi_1 = 7.1°$, $\varphi_2 = 43.9°$), with geometric data similar to the values reported by Bordner and Andrews [12] for a sample of $(Ph_2Sb)_2O$, which presumably was obtained by hydrolysis of Ph_2SbCl. In contrast, both tolyl compounds adopt conformations close to *syn–anti* ((o-$Tol_2Sb)_2O$: $\varphi_1 = 36.0°$, $\varphi_2 = 160.3°$; (p-$Tol_2Sb)_2O$: $\varphi_1 = 7.4°$, $\varphi_2 = 172.7°$). This unspecific distribution of torsional angles φ suggests that the conformations of the molecules are almost equal in energy. For $(R_2Sb)_2O$ (R = Ph, *o*-Tol, *p*-Tol) the differences in energy between the various conformations are not known. Calculations for $(Me_2Sb)_2O$ revealed that the *syn–anti* conformer is only 4.6 kJ mol^{-1} higher in energy than the *syn–syn* form [10]. Almost equal amounts of both conformers are present in the gas phase [10]. In crystals of $(Me_2Sb)_2O$, however, the *syn–anti* conformation is adopted exclusively. This preference results from the association of the molecules through intermolecular Sb···O contacts with the formation of a $[(Me_2Sb)_2O]_x$ chain [11]. In crystals of $(R_2Sb)_2O$ (R = Ph, *o*-Tol, *p*-Tol) the molecules are only loosely packed to stacks without unusual contacts between them (intermolecular Sb–Sb distances ≥ 520.5(4) pm). Consequently the packing forces are weak and a relatively wide distribution of dihedral angles results.

The Sb–O bond lengths of $(R_2Sb)_2O$ (R = Ph, 197.1(3), 197.8(3); R = *o*-Tol, 196.7(2), 197.8(2); R = *p*-Tol, 196.7(4), 198.6(4) pm lie in the range for single bonds not involved in intermolecular interactions, cf. $(Me_2Sb)_2O$, 198.8(5) [11]; $(RSbO)_4$ (R = $(Me_3Si)_2CH$), 196.8(3), 197.0(3) pm [13]. The Sb–O–Sb angle in the $(R_2Sb)_2O$ molecules is a little wider for the *o*-tolyl derivative (126.5(1)°) than for the phenyl (121.4(2)°), or *p*-tolyl (122.2(2)°) compound. Similar values were found for $(Me_2Sb)_2O$ (123.0(3)) [11] and $(RSbO)_4$ (R = $(Me_3Si)_2CH$) (122.3(2)°) [13].

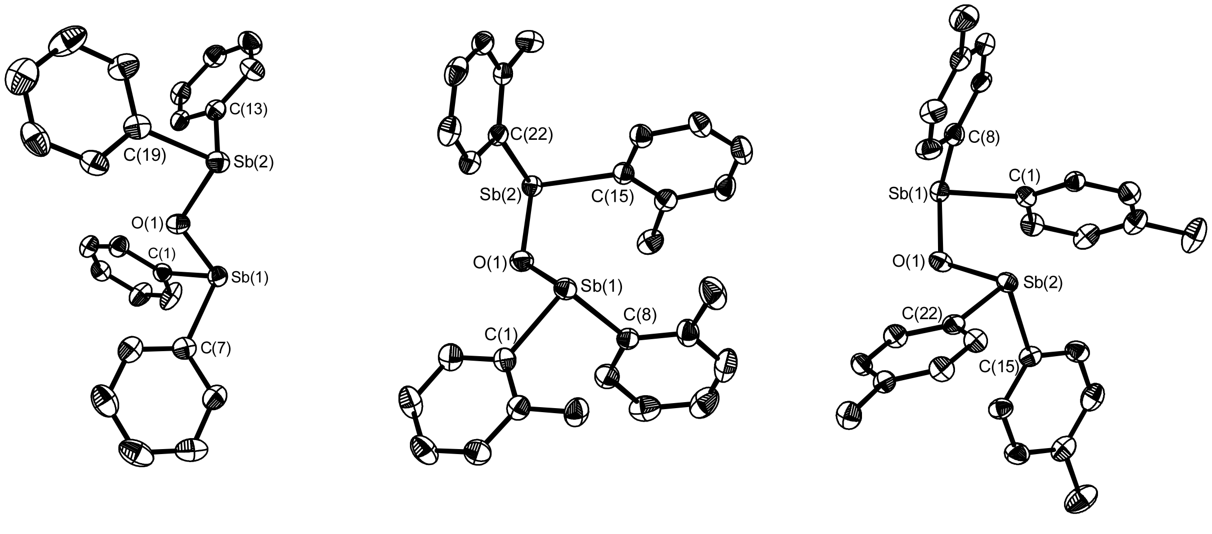


Fig. 1. Left: structure of $(Ph_2Sb)_2O$, distances (pm) and angles (°), Sb(1)–O(1) 197.8(3), Sb(2)–O(1) 197.1(3); Sb(1)–C(1) 215.6(5), Sb(1)–C(8) 214.3(4); Sb–O–Sb 121.4(2). Centre: structure of (o-$Tol_2Sb)_2O$, Sb(1)–O(1) 197.8(2), Sb(2)–O(1) 196.7(2); Sb(1)–C(1) 215.5(3), Sb(1)–C(8) 215.4(3), Sb(2)–C(15) 216.9(3), Sb(2)–C(22) 215.0(3); Sb–O–Sb 126.5(1). Right: structure of p-Tol_2Sb_2O, Sb(1)–O(1) 196.7(4), Sb(2)–O(1) 198.6(4); Sb(1)–C(1) 213.6(5), Sb(1)–C(8) 215.0(5), Sb(2)–C(15) 215.6(5), Sb(2)–C(22) 214.6(5); Sb–O–Sb 122.2(2).

Table 1
Crystal data and structure refinement parameters

	$(Ph_2Sb)_2O$	$(o\text{-}Tol_2Sb)_2O$	$(p\text{-}Tol_2Sb)_2O$	$(Ph_2SbO)_4(O_2)_2$
Empirical formula	$C_{24}H_{20}OSb_2$	$C_{28}H_{28}OSb_2$	$C_{28}H_{28}OSb_2$	$C_{48}H_{40}O_8Sb_4$
Formula mass (g mol^{-1})	567.90	624.00	624.00	1231.80
Colour	Colourless	Colourless	Colourless	Colourless
Crystal size (mm)	0.6 × 0.4 × 0.4	0.6 × 0.4 × 0.4	0.7 × 0.4 × 0.4	0.5 × 0.4 × 0.4
Radiation (pm)	71.073	71.073	71.073	71.073
Temperature (K)	173(2)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$Pna2_1$	$P2_1/c$
Unit cell dimensions				
a (pm)	591.5(1)	827.7(1)	1460.7(2)	1356.6(3)
b (pm)	2976.2(3)	1105.0(2)	2776.1(3)	1754.6(4)
c (pm)	1201.4(1)	147.8(3)	611.3(1)	1876.1(3)
α (°)	90	87.69(2)	90	90
β (°)	95.26(1)	82.37(2)	90	98.97(2)
γ (°)	90	68.85(2)	90	90
V (nm^3)	2.1061(5)	1.2494(4)	2.4789(6)	4.411(2)
Z	4	2	4	4
ρ_{calc} (g cm^{-3})	1.791	1.659	1.672	1.855
μ (mm^{-1})	2.576	2.179	2.196	2.477
θ Range (°)	2.67–27.50	2.66–27.49	2.61–27.50	2.57–27.50
Reflections collected	5907	6349	6736	20 315
Independent reflections	4234 ($R_{int} = 0.0293$)	5094 ($R_{int} = 0.0218$)	3250 ($R_{int} = 0.0382$)	10 127 ($R_{int} = 0.0364$)
Parameters refined	246	287	287	543
R_1	0.0337	0.0261	0.0269	0.0396
wR_2	0.0776	0.0685	0.0659	0.0888
R indices (all data)	$R_1 = 0.0491$, $wR_2 = 0.0776$	$R_1 = 0.0307$, $wR_2 = 0.0685$	$R_1 = 0.0300$, $wR_2 = 0.0659$	$R_1 = 0.0732$, $wR_2 = 0.0888$
Largest difference peak and hole (e Å^{-3})	1.138 and −0.686	1.035 and −0.531	0.747 and −0.660	0.806 and −0.815
Absorption correction	DIFABS [16]	DIFABS [16]	DIFABS [16]	DIFABS [16]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Diffractometer	Siemens P4	Siemens P4	Siemens P4	Siemens P4

2.2. Synthesis of $(R_2Sb)_4O_6$ and $(R_2SbO)_4(O_2)_2$ ($R = Ph$, o-Tol, p-Tol)

Injection of a flow of air into solutions of distibanes, $(R_2Sb)_2$ or monoxides, $(R_2Sb)_2O$, in diethyl ether or other organic solvents leads to complete oxidation with precipitation of tetrakis(diarylantimony)hexoxides, $(R_2Sb)_4O_6$ (R = Ph, *o*-Tol, *p*-Tol). The hexoxides (stibinic acid anhydrides) are white air stable solids, insoluble in organic solvents and water.

$$2(R_2Sb)_2O + 2O_2 \rightarrow (R_2Sb)_4O_6 \quad R = Ph, o\text{-}Tol, p\text{-}Tol \tag{2}$$

The identity of the hexoxides was proved by elemental analyses and mass spectroscopy. Molecular ions were obtained by chemical ionization techniques. Electron impact spectra contain signals of the fragments $M^+ - R$ at highest mass. Attempts to grow crystals failed due to the low solubility of the compounds. Single crystals of $(Ph_2Sb)_4O_6$ [6] and $(o\text{-}Tol_2Sb)_4O_6$ [7] suitable for X-ray analysis were obtained from other sources and their structures were reported.

Addition of excess H_2O_2 to $(R_2Sb)_4O_6$ results in the formation of the peroxo clusters $(R_2SbO)_4(O_2)_2$ (R = Ph, *o*-Tol [5], *p*-Tol) as white crystalline solids, which in contrast to the hexoxides that are very well soluble in organic solvents. The crystals are stable for a long time. Solutions decompose after several weeks at room temperature.

$$(R_2Sb)_4O_6 + 2H_2O_2 \rightarrow (R_2SbO)_4(O_2)_2 + 2H_2O$$
$$R = Ph, o\text{-}Tol, p\text{-}Tol \tag{3}$$

Mass spectra obtained with the chemical ionization technique contain the molecular ions as the most intensive signals. The ^{1}H-NMR spectra show that all phenyl groups have equivalent positions. The crystal structure of $(Ph_2SbO)_4(O_2)_2$ was determined by X-ray structure analysis on single crystals obtained from a solution in toluene at −23 °C. The crystallographic data are given in Table 1. A view of the molecular structure is depicted in Fig. 2. The structure contains a puckered $(SbO)_4$ ring, where antimony atoms approximately occupy the corners of a square. Two mutually perpendicular O–O units are in capping positions above and below the plane of the antimony atoms closing the antimony oxygen cage.

The good solubility and the relative high thermal stability of the molecules may be explained by the coordinative saturation of the atoms in the cage and by the shielding through the external phenyl groups. The O–O bond lengths of the peroxide bridges (mean 147 pm) as well as the Sb–O distances in the $(SbO)_4$ ring (mean 196 pm) correspond to normal single bonds. The distances between the antimony atoms and the oxygen atoms of the peroxide groups (mean 223 pm) are longer. As expected, there are only subtle differences between the structures of the phenyl- and the *o*-tolyl compound [5]. Attempts to use these compounds as sources for $^1O_2$ have not yet been successful.

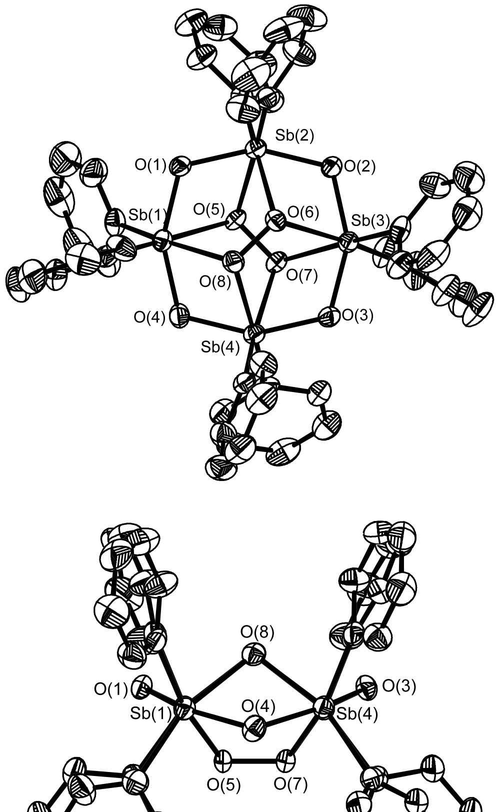


Fig. 2. Two views on the structure of $(Ph_2SbO)_4(O_2)_2$, (below: O(2), O(4) and O(6), O(8) are in ecliptic positions) distances (pm) and angles (°): Sb–O(O) 220.5(3)–225.1(3), Sb–C 210.3(5)–212.4(5), Sb–O(Sb) 194.6(3)–197.6(3), O(5)–O(7) 146.1(4), O(6)–O(8) 146.6(5); Sb–O(Sb)–Sb 110.89(1)–111.91(1), Sb–O(O)–Sb 92.9(1)–93.54(1), Sb–O(O)–O(O) 112.8(2)–114.2(2), O(O)–Sb–O(O) 74.51(1)–74.91(1), C–Sb–C 105.8(2)–108.1(2). O(Sb)–Sb–O(Sb) 153.96(1)–154.61(1), O(Sb)–Sb–C 92.6(2)–103.6(2), O(Sb)–Sb–O(O) 74.13(1)–75.26(1), O(O)–Sb–C 87.5(1)–91.9(2), O(Sb)–Sb–O(O) 83.95(1)–85.51(1), O(O)–Sb–C 159.6(2)–164.8(2).

3. Experimental

The experiments were performed in an Ar atmosphere, using dried solvents distilled under Ar. Ph_4Sb_2 [8], *o*-Tol_3Sb [14] and *p*-Tol_3Sb [15] were prepared as reported.

3.1. Synthesis of tetratolyldistibanes

(a) *o*-Tol_4Sb_2: 15.8 g (40 mmol) *o*-Tol_3Sb was added to a solution of 1.84 g (80 mmol) Na in 150 ml liquid NH_3 at −70 °C and the mixture was stirred for 1.5 h. The solution became dark red and 7.49 g (40 mmol) $BrCH_2CH_2Br$ was added dropwise through a syringe. After stirring for 1 h NH_3 was allowed to evaporate. The remaining yellow solid was washed with 150 ml water, dried at reduced pressure and dissolved in 100 ml Et_2O. Cooling the yellow solution to −23 °C gave 3.46 g (28.5%) yellow crystals of *o*-Tol_4Sb_2 (m.p. 158 °C). ^1H-NMR ($CDCl_3$): $\delta = 2.48$ (s, 3H, CH_3) 7.05–7.24, 7.39–7.41 (m, 4H, C_6H_4). MS (70 eV), *m*/*z* (%): 607 (45) [M^+], 303 (95) [Tol_2Sb^+], 182 (100) [Tol_2^+]. Anal. Found: C, 55.72; H, 4.72. Calc. for $C_{28}H_{28}Sb_2$: C, 55.31; H, 4.64%. (b) *p*-Tol_4Sb_2: the analogous procedure with 15.8 g *p*-Tol_3Sb gave 3.82 g (31.5%) yellow *p*-Tol_4Sb_2 (m.p. 155 °C). ^1H-NMR ($CDCl_3$): $\delta = 2.36$ (s, 3H, CH_3), 7.20–7.27, 7.43–7.49 (AA′XX′ spin system, 4H, C_6H_4). MS (70 eV), *m*/*z* (%): 607 (52) [M^+], 303 (100) [Tol_2Sb^+], 182 (90) [Tol_2^+]. Anal. Found: C, 54.18; H, 4.56. Calc. for $C_{28}H_{28}Sb_2$: C, 55.31; H, 4.64%.

3.2. Synthesis of bis(diarylantimony)oxides

(a) $(Ph_2Sb)_2O$: A solution of 2.00 g (3.63 mmol) Ph_4Sb_2 in 100 ml Et_2O was exposed to the air until the yellow colour of the distibane had almost disappeared. Removal of the solvent at reduced pressure gave 1.93 g (94%) $(Ph_2Sb)_2O$ as a colourless solid. Single crystals (m.p. 78 °C, Ref. [1]: 78–81 °C) were grown from a solution in Et_2O exposed to the atmosphere at room temperature. ^1H-NMR ($CDCl_3$): $\delta = 7.40$–7.45 (m, 3H, C_6H_5), 7.61–7.66 (m, 2H, C_6H_5). MS data as reported in Ref. [1]. (b) (*o*-$Tol_2Sb)_2O$: the analogous reaction of 2.00 g (3.29 mmol) *o*-Tol_4Sb_2 in 100 ml Et_2O gave 1.98 g (96%) of white solid (*o*-$Tol_2Sb)_2O$ (m.p. 109 °C). Single crystals were grown in toluene at −23 °C. ^1H-NMR ($CDCl_3$): $\delta = 2.25$ (s, 3H, CH_3) 7.06–7.25, 7.58–7.65 (m, 4H, C_6H_4), MS (70 eV); *m*/*z* (%): 624 (96) [M^+], 533 (43) [$M^+ - Tol$], 441 (10) [$M^+ - 2Tol$], 303 (56), 212 (39) 181 (95), 91(100). (c) *p*-Tol_4Sb_2O: the air oxidation of 2.00 g (3.29 mmol) *p*-Tol_4Sb_2 in 100 ml Et_2O gave 2.05 g (100%) of white solid (*p*-$Tol_2Sb)_2O$ (m.p. 101 °C, Ref. [3]: 101 °C). Single crystals were grown in toluene at −23 °C. ^1H-NMR ($CDCl_3$): $\delta =$ 2.33 (s, 3H, CH_3) 7.10–7.17, 7.38–7.42 (AA′XX′ spin system, 4H, C_6H_4). MS (70 eV); *m/z* (%): 624 (54) [M^+], 533 (42), 442 (83), 394 (41), 303 (83), 212 (87), 182 (100), 91(82).

3.3. Synthesis of tetrakis(diarylantimony)hexoxides by the oxidation of distibanes

(a) $(Ph_2Sb)_4O_6$: 3.00 g (5.44 mmol) Ph_4Sb_2 was dissolved in 150 ml Et_2O and a gentle flow of dry air was passed through the solution until the yellow colour of the solution disappeared and the precipitation of a white solid was completed. Washing of the precipitate with Et_2O and removal of the solvent at reduced pressure gave 3.13 g (95.9%) $(Ph_2Sb)_4O_6$ as white solid powder (m.p. 280 °C, Ref. [6]: 285–290 °C). EIMS (280 °C, 70 eV); *m/z* (%): 1123 (2) [$M^+ - Ph$], 429 (8), 352 (10), 275 (19), 198 (81), 154 (100), 77 (43) Ph; MS (DCI neg., NH_3); *m/z* (%): 1223 (100) [$M^- - Ph$], 1047 (41). (b) $(o\text{-}Tol_2Sb)_4O_6$: 3.00 g (4.93 mmol) $o\text{-}Tol_4Sb_2$ reacted with air in an analogous procedure to give 3.01 g (93.0%) $(o\text{-}Tol_2Sb)_4O_6$ as a white powder (m.p. 266 °C). MS (DCI neg., NH_3) *m/z* (%): 1221 (100) [$M^- - Tol$], 395 (76), 319 (25). Anal. Found: C, 51.26; H, 3.62. Calc. for $C_{56}H_{56}O_6Sb_4$: C, 51.26; H, 4.30%. (c) $(p\text{-}Tol_2Sb)_4O_6$: 3.00 g (4.93 mmol) $p\text{-}Tol_4Sb_2$ was reacted with air in 150 ml of Et_2O to give 3.05 g (94.4%) $(p\text{-}Tol_2Sb)_4O_6$ as white solid powder (m.p. 280 °C). MS (DCI neg., NH_3) *m/z* (%): 1221 (100) [$M^+ - Tol$], 395 (28), 319 (55), 303 (5). Anal. Found: C, 50.87; H, 4.07. Calc. for $C_{56}H_{56}O_6Sb_4$: C, 51.26; H, 4.30%.

3.4. Synthesis of tetrakis(diarylantimony)di-μ_4-peroxo-tetroxides

(a) $(Ph_2SbO)_4(O_2)_2$: 100 ml of a 30% aqueous solution (0.98 mol) of H_2O_2 was added to a suspension of 3.60 g (3.0 mmol) $(Ph_2Sb)_4O_6$ in 100 ml Et_2O and the mixture was stirred for 4 h. Washing the precipitate with water and Et_2O and drying under reduced pressure gave 3.37 g (91.3%) $(Ph_2SbO)_4(O_2)_2$ as white powder (m.p. (dec.) 293 °C). Single crystals were obtained from a solution in toluene at -23 °C after 2 months. ^{1}H-NMR (C_6D_6): $\delta = 6.97–7.03$ (m, 3H), 8.02–8.08 (m, 2H) MS (DCI pos., NH_3); *m/z* (%): 1233 (100) [$M^+ + H$]. Anal. Found: C, 46.44; H, 3.63. Calc. for $C_{48}H_{40}O_8Sb_4$: C, 46.80; H, 3.27%. (b) $(o\text{-}Tol_2Sb)_4O_6$: 3.94 g (3.0 mmol) $(o\text{-}Tol_2Sb)_4O_6$ in 100 ml Et_2O and 100 ml of a 30% aqueous solution (0.98 mol) of H_2O_2 reacted to give 3.78 g (93.7%) $(o\text{-}Tol_2SbO)_4(O_2)_2$ as white powder (m.p. (dec.) 273 °C). ^{1}H-NMR (C_6D_6): $\delta = 2.45$ (s, 3H), 6.75 (t, $^3J = 3$ Hz, 1H), 6.92 (d, $^3J = 8$ Hz, 1H), 7.00 (t, $^3J = 3$ Hz, 1H), 7.93 (d, $^3J = 8$ Hz, 1H). MS (DCI pos., NH_3); *m/z* (%): 1345 (100) [$M^+ + H$]. Anal. Found: C, 50.39; H, 4.70. Calc. for $C_{56}H_{56}O_8Sb_4$: C, 50.04; H, 4.20%. (c) $(p\text{-}Tol_2SbO)_4(O_2)_2$: 3.94 g (3.0 mmol) $(p\text{-}Tol_2Sb)_4O_6$ in 100 ml Et_2O and 100 ml of a 30% aqueous solution (0.98 mol) of H_2O_2 reacted to give 3.72 g (92.4%) $(p\text{-}Tol_2SbO)_4(O_2)_2$ as a white powder (m.p. (dec.), 281 °C). ^{1}H-NMR (C_6D_6): $\delta = 1.92$ (s, 3H, CH_3), 6.8–6.9, 8.0–8.1 (m, 4H, C_6H_4). MS (DCl pos., NH_3); *m/z* (%): 1345 (100) [$M^+ + H$]. Anal. Found: C, 51.02; H, 4.76. Calc. for $C_{56}H_{56}O_8Sb_4$: C, 50.04; H, 4.20%.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 168018, 168015–168017 for $(Ph_2Sb)_2O$, $(o\text{-}Tol_2Sb)_2O$, $(p\text{-}Tol_2Sb)_2O$, $(Ph_2SbO)_4(O_2)_2$, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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