Synthesis, characterization and crystal structures of tri- and tetraphenylantimony(V) compounds containing arylcarbonyloxy moiety

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ABSTRACT

A series of tri- and tetraphenylantimony(V) compounds containing arylcarbonyloxy moiety have been synthesized and characterized by elemental analysis, IR, and NMR spectroscopy. Attempts to grow crystals led to colorless blocks identified by X-ray diffraction as $(ArCOO)_2SbPh_3$ or $(ArCOO)SbPh_4$.

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1. Introduction

The chemistry of antimony compounds derived from carboxylates have been an active area of research for more than eight decades [1,2], not only for the striking structural possibilities ranging from discrete monomeric structures to supramolecular assemblies [3], but also for the biological importance [4] in antimicrobial properties [5] as well as antitumor activities [6,7]. A great number of references describing synthesis and biological activities of organoantimony carboxylates with the general formula R_nSbX_{5-n} (R = alkyl, aryl; n = 3, 4; X = carboxylate) have already appeared in the literature [8–29]. The published data on the antitumor activity of these compounds, however, are relatively limited [30,22]. In the present paper we have prepared a series of arylantimony derivatives of arylcarboxylic acid. We are interested in studying the nature of bonding and structural information of these compounds. The general reaction scheme is shown in Scheme 1.

2. Experimental

2.1. Materials and instrumentation

Solvents were dried and distilled before use. The elemental analyses were performed on a PE-2400-II elemental analyzer. IR spectra were recorded on a Nicolet-460 spectrophotometer, as KBr discs. X-ray measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. ^{1}H and ^{13}C NMR (CDCl$_3$): δ spectra were recorded on Varian Mercury Plus-400 NMR spectrometer and the chemical shifts were reported in ppm relative to tetramethylsilane (TMS) in CDCl$_3$.

2.2. Syntheses of compounds 1–12

#### 2.2.1. Preparation of $Ph_3Sb(Cl)(O_2C-C_9H_6N)$ (**1**)

2-Quinoline carboxylic acid (0.069 g, 0.4 mmol) and sodium methoxide (0.4 mmol) were added with stirring to solution containing triphenylantimony dichloride (0.172 g, 0.4 mmol) in toluene (30 ml). After refluxing for 8 h, the colorless solution was obtained and then filtered. The solvent was gradually removed by evaporation under vacuum until the white solid was obtained. The solid was recrystallized from petroleum ether/dichloromethane (1:4) to give colorless crystals. Yield 63%, m.p. 129–131 °C. Anal. Calc. for $C_{28}H_{21}NClO_2Sb$ (560.68): C, 59.98; H, 3.77; O, 5.71. Found: C, 59.72; H, 3.68; O, 5.53%. IR (KBr, cm^{-1}): 1669 (C=O), 1647 (C=N), 1367 (C–O), 593 (Sb–N), 456 (Sb–O), 445 (Sb–C). ^{1}H NMR (CDCl$_3$): δ 7.38 (9H, m, *m*- and *p*-Ph), 7.98 (6H, m, *o*-Ph), 7.55 (1H, d, J = 4 Hz, 10-quinoline-H), 7.83 (1H, d, J = 4 Hz, 7-quinoline-H), 9.24 (1H, d, J = 4 Hz, 4-quinoline-H), 8.20 (2H, m, 8,9-quinoline-H), 8.62 (1H, m, 3-quinoline-H). ^{13}C NMR (CDCl$_3$): δ 127.2, 128.3, 134.1, 136.9 (Ph–Sb); 121.5, 127.4, 127.9, 129.1, 129.6, 131.7, 137.1, 148.4, 154.2 (C_9H_6N); 167.8 (C=O).

2.2.2. Preparation of $Ph_3Sb(O_2C-C_9H_6N)_2$ (**2**)

2-Quinoline carboxylic acid (0.072 g, 0.42 mmol) and sodium methoxide (0.42 mmol) were added with stirring to solution

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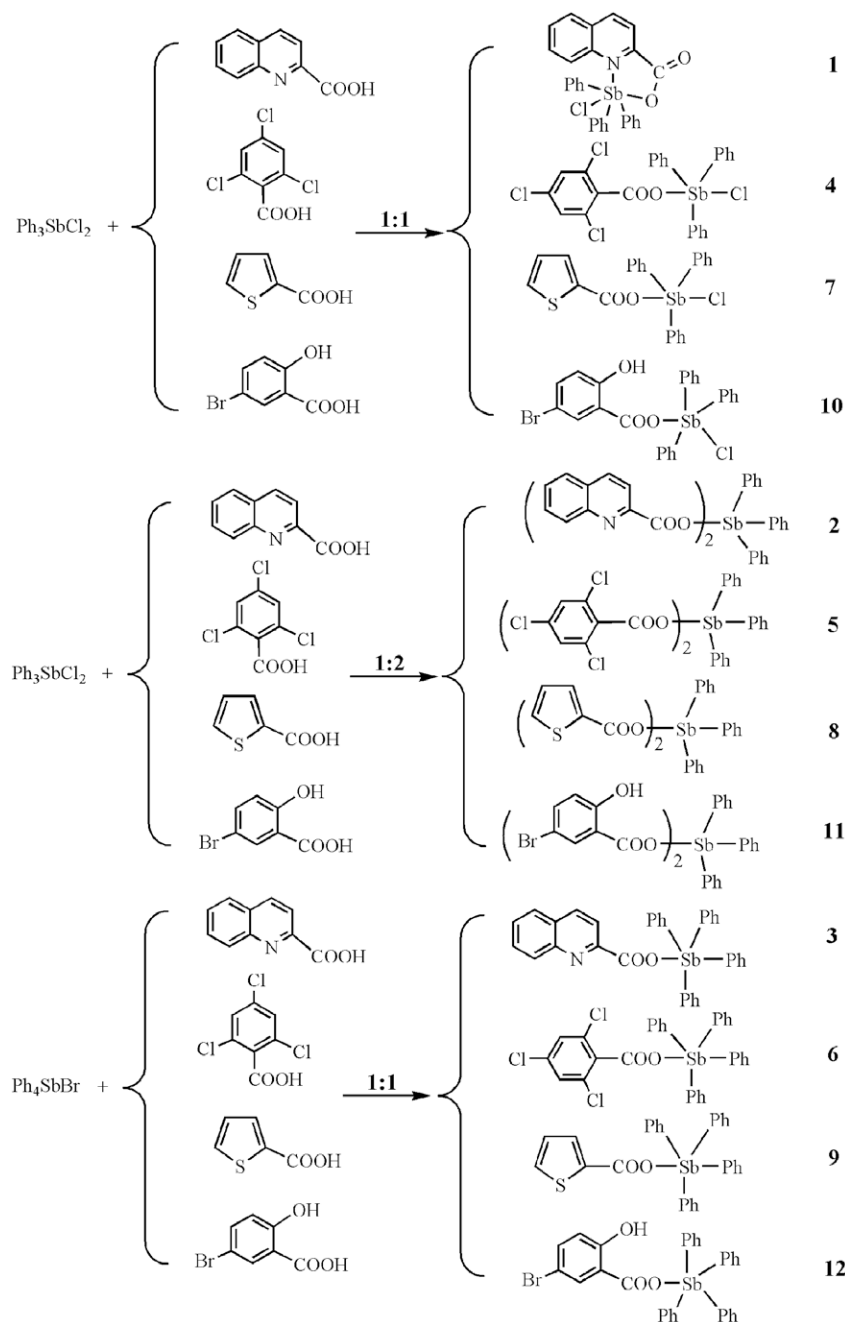
Scheme 1.

containing triphenylantimony dichloride (0.086 g, 0.2 mmol) in toluene (30 ml). After refluxing for 8 h, the colorless solution was obtained and then filtered. The solvent was gradually removed by evaporation under vacuum until the white solid was obtained. The solid was recrystallized from petroleum ether/dichloromethane (1:1) to give colorless crystals. Yield 60%, m.p. 130–133 °C. Anal. Calc. for $C_{38}H_{27}N_2O_4Sb$ (697.39): C, 65.44; H, 3.90; O, 9.18. Found: C, 65.21; H, 4.12; O, 9.39%. IR (KBr, cm^{-1}): 1700 (C=O), 1682 (C=N), 1402 (C–O), 478 (Sb–O), 451 (Sb–C). ^{1}H NMR (CDCl$_3$): δ 7.56 (9H, m, *m*- and *p*-Ph), 8.13 (6H, m, *o*-Ph), 7.83 (2H, d, *J* = 4 Hz, 10-quinoline-H), 8.21 (2H, d, *J* = 4 Hz, 7-quinoline-H), 9.12 (2H, d, *J* = 4 Hz, 4-quinoline-H), 8.34 (4H, m, 8,9-quinoline-H), 8.85 (2H, m, 3-quinoline-H). ^{13}C NMR (CDCl$_3$): δ 129.4, 130.3, 135.6, 139.7 (Ph–Sb); 121.6, 128.7, 129.9, 130.6, 131.3, 132.0, 138.6, 147.9, 153.8 (C$_9$H$_6$N); 170.0 (C=O).

2.2.3. Preparation of Ph$_4$Sb(O$_2$C–C$_9$H$_6$N) (3)

2-Quinoline carboxylic acid (0.076 g, 0.44 mmol) and sodium methoxide (0.44 mmol) were added with stirring to solution containing teraphenylantimony bromide (0.204 g, 0.4 mmol) in toluene (30 ml). After refluxing for 8 h, the colorless solution was obtained and then filtered. The solvent was gradually removed by evaporation under vacuum until the white solid was obtained. The solid was recrystallized from petroleum ether/dichloromethane (1:1) to give colorless crystals. Yield 60%, m.p. 128–132 °C. Anal. Calc. for $C_{34}H_{26}O_2NSb$ (602.33): C, 67.80; H, 4.35; O, 5.31. Found: C, 67.59; H, 4.59; O, 5.53%. IR (KBr, cm^{-1}): 1678 (C=N), 1660 (C=O), 1345 (C–O), 462 (Sb–O), 450 (Sb–C). ^{1}H NMR (CDCl$_3$): δ 7.45 (12H, m, *m*- and *p*-Ph), 8.08 (8H, m, *o*-Ph), 7.61 (1H, d, *J* = 5 Hz, 10-quinoline-H), 7.78 (1H, d, *J* = 4 Hz, 7-quinoline-H), 9.13 (1H, d, *J* = 4 Hz, 4-quinoline-H), 8.28 (2H, m, 8,9-quinoline-

H), 8.57 (1H, m, 3-quinoline-H). ^{13}C NMR (CDCl$_3$): δ 128.1, 130.7, 133.2, 138.9 (Ph–Sb); 122.3, 127.7, 128.6, 129.5, 131.1, 132.4, 137.1, 149.6, 158.7 (C$_9$H$_6$N); 172.4 (C=O).

2.2.4. Preparation of Ph$_3$Sb(Cl)[O$_2$C–C$_6$H$_2$Cl$_3$] (4)

Compound **4** was prepared in the same way as **1**. The solid was recrystallized from petroleum ether/dichloromethane (1:1) to give colorless crystals. Yield 68%, m.p. 129–132 °C. Anal. Calc. for C$_{25}$H$_{17}$O$_2$Cl$_4$Sb (612.97): C, 48.99; H, 2.80; O, 5.22. Found: C, 48.77; H, 2.98; O, 5.43%. IR (KBr, cm^{-1}): 1710 (C=O), 1455 (C–O), 501 (Sb–O), 478 (Sb–C). ^{1}H NMR (CDCl$_3$): δ 7.36–8.83 (m, Ph, 17H). ^{13}C NMR (CDCl$_3$): δ 128.8, 133.1, 136.4, 139.7 (C$_6$H$_5$); 129.7, 131.9, 136.2, 140.4, 144.7, 148.2 (C$_6$H$_3$Cl$_3$); 179.6 (C=O).

2.2.5. Preparation of Ph$_3$Sb[O$_2$C–C$_6$H$_2$Cl$_3$]$_2$ (5)

Compound **5** was prepared in the same way as **2**. The solid was recrystallized from petroleum ether/dichloromethane (1:1) to give colorless crystals. Yield 65%, m.p. 150–152 °C. Anal. Calc. for C$_{65}$H$_{42}$Cl$_{12}$O$_9$Sb$_2$ (1635.97): C, 47.72; H, 2.59; O, 8.80. Found: C, 47.41; H, 2.73; O, 9.11%. IR (KBr, cm^{-1}): 1692 (C=O), 1353 (C–O), 471 (Sb–O), 459 (Sb–C). ^{1}H NMR (CDCl$_3$): δ 2.12 (3H, s, CH$_3$–O), 4.24 (1H, m, OH), 7.43–8.69 (38H, m, Ph). ^{13}C NMR (CDCl$_3$): δ 127.7, 132.6, 135.7, 140.2 (C$_6$H$_5$); 129.7, 132.6, 135.7, 139.8, 142.6, 147.7 (C$_6$H$_3$Cl$_3$); 177.9 (C=O).

2.2.6. Preparation of Ph$_4$Sb[O$_2$C–C$_6$H$_2$Cl$_3$] (6)

Compound **6** was prepared in the same way as **3**. The solid was recrystallized from petroleum ether/dichloromethane (1:1) to give colorless crystals. Yield 61%, m.p. 131–133 °C. Anal. Calc. for C$_{31}$H$_{22}$O$_2$Cl$_3$Sb (654.62): C, 56.88; H, 3.39; O, 4.89. Found: C, 56.69; H, 3.55; O, 5.01%. IR (KBr, cm^{-1}): 1687 (C=O), 1359 (C–O), 466 (Sb–O), 454 (Sb–C). ^{1}H NMR (CDCl$_3$): δ 7.38–8.75 (22H, m, Ph). ^{13}C NMR (CDCl$_3$): δ 127.9, 133.0, 136.2, 142.8 (C$_6$H$_5$); 129.8, 132.4, 136.7, 140.9, 143.5, 149.0 (C$_6$H$_3$Cl$_3$); 182.7 (C=O).

2.2.7. Preparation of Ph$_3$Sb(Cl)(O$_2$C–C$_4$H$_3$S) (7)

Compound **7** was prepared in the same way as **1**. The solid was recrystallized from petroleum ether/dichloromethane (1:1) to give colorless crystals. Yield 80%, m.p. 119–122 °C. Anal. Calc. for C$_{23}$H$_{18}$O$_2$SClSb (515.66): C, 53.57; H, 3.52; O, 6.21; S, 6.22. Found: C, 53.35; H, 3.73; O, 6.43; S, 6.41%. IR (KBr, cm^{-1}): 1712 (C=O), 1402 (C–O), 489 (Sb–O), 467 (Sb–C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.23–7.89 (3H, m, C$_4$H$_3$S), 7.25–8.22 (15H, m, C$_6$H$_5$). ^{13}C NMR (CDCl$_3$): δ (100 MHz, CDCl$_3$): 121.6, 126.8, 127.4, 128.1, 128.8, 129.9, 130.7, 135.6, 137.5 (C$_4$H$_3$S, Ph); 175.6 (C=O).

2.2.8. Preparation of Ph$_3$Sb(O$_2$C–C$_4$H$_3$S)$_2$ (8)

Compound **8** was prepared in the same way as **2**. The solid was recrystallized from petroleum ether/dichloromethane (1:1) to give colorless crystals. Yield 87%, m.p. 130–132 °C. Anal. Calc. for C$_{28}$H$_{21}$O$_4$S$_2$Sb (607.35): C, 55.37; H, 3.48; O, 10.53; S, 10.56. Found: C, 55.12; H, 3.69; O, 10.79; S, 10.80%. IR (KBr, cm^{-1}): 1701 (C=O), 1325 (C–O), 461 (Sb–O), 451 (Sb–C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.89–7.54 (6H, m, C$_4$H$_3$S), 7.39–8.01 (15H, m, C$_6$H$_5$). ^{13}C NMR (CDCl$_3$): δ (100 MHz, CDCl$_3$): 121.4, 126.5, 127.4, 128.0, 128.9, 129.8, 130.4, 136.4, 138.3 (C$_4$H$_3$S, Ph); 172.3 (C=O).

2.2.9. Preparation of Ph$_4$Sb(O$_2$C–C$_4$H$_3$S) (9)

Compound **9** was prepared in the same way as **3**. The solid was recrystallized from petroleum ether/dichloromethane (1:1) to give colorless crystals. Yield 87%, m.p. 123–125 °C. Anal. Calc. for C$_{29}$H$_{23}$O$_2$SSb (557.31): C, 62.50; H, 4.16; O, 5.74; S, 2.75. Found: C, 62.31; H, 4.38; O, 5.96; S, 7.56%. IR (KBr, cm^{-1}): 1694 (C=O), 1331 (C–O), 467 (Sb–O), 456 (Sb–C). ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.82–7.70 (3H, m, C$_4$H$_3$S), 7.41–8.12 (20H, m, C$_6$H$_5$). ^{13}C NMR

(CDCl$_3$): δ (100 MHz, CDCl$_3$): 122.10, 125.89, 127.33, 128.05, 128.86, 129.08, 132.23, 137.36, 139.21 (C$_4$H$_3$S, Ph); 174.8 (C=O).

2.2.10. Preparation of Ph$_3$Sb(Cl)[O$_2$C–C$_6$H$_3$(OH)(Br)] (10)

Compound **10** was prepared in the same way as **1**. The solid was recrystallized from petroleum ether/dichloromethane (1:1) to give colorless crystals. Yield 73%, m.p. 128–131 °C. Anal. Calc. for C$_{25}$H$_{19}$ClO$_3$BrSb (604.53): C, 49.67; H, 3.17; O, 7.94. Found: C, 49.46; H, 3.35; O, 8.13%. IR (KBr, cm^{-1}): 1697 (C=O), 1395 (C–O), 478 (Sb–O), 452 (Sb–C). ^{1}H NMR (CDCl$_3$): δ 7.20–8.68 (18H, m, Ph); 9.10 (1H, s, Ph–OH). ^{13}C NMR (CDCl$_3$): δ 129.1, 132.4, 135.9, 141.1 (C$_6$H$_5$); 129.8, 133.5, 137.8, 140.3, 141.9, 143.0 (C$_6$H$_3$); 175.5 (C=O).

2.2.11. Preparation of Ph$_3$Sb[O$_2$C–C$_6$H$_3$(OH)(Br)]$_2$ (11)

Compound **11** was prepared in the same way as **2**. The solid was recrystallized from petroleum ether/dichloromethane (1:1) to give colorless crystals. Yield 71%, m.p. 142–144 °C. Anal. Calc. for C$_{32}$H$_{23}$O$_6$Br$_2$Sb (785.08): C, 48.96; H, 2.95; O, 12.23. Found: C, 48.73; H, 3.13; O, 12.41%. IR (KBr, cm^{-1}): 1670 (C=O), 1349 (C–O), 454 (Sb–O), 443 (Sb–C). ^{1}H NMR (CDCl$_3$): δ 7.13–8.41 (21H, m, Ph); 9.12 (2H, s, Ph–OH). ^{13}C NMR (CDCl$_3$): δ 127.6, 130.7, 135.7, 140.9 (C$_6$H$_5$); 129.6, 131.7, 137.7, 139.9, 140.7, 142.3 (C$_6$H$_3$); 170.5 (C=O).

2.2.12. Preparation of Ph$_4$Sb[O$_2$C–C$_6$H$_3$(OH)(Br)] (12)

Compound **12** was prepared in the same way as **3**. The solid was recrystallized from petroleum ether/dichloromethane (1:1) to give colorless crystals. Yield 66%, m.p. 131–134 °C. Anal. Calc. for C$_{31}$H$_{24}$O$_3$BrSb (646.18): C, 57.62; H, 3.74; O, 7.43. Found: C, 57.41; H, 3.92; O, 7.61%. IR (KBr, cm^{-1}): 1679 (C=O), 1341 (C–O), 458 (Sb–O), 447 (Sb–C). ^{1}H NMR (CDCl$_3$): δ 7.14–8.43 (23H, m, Ph); 9.08 (1H, s, Ph–OH). ^{13}C NMR (CDCl$_3$): δ 126.1, 131.2, 134.8, 141.7 (C$_6$H$_5$); 129.9, 132.6, 136.8, 140.9, 142.5, 144.6 (C$_6$H$_3$); 175.9 (C=O).

2.3. Crystal structure determination and refinement

Single crystals suitable for X-ray analysis were mounted in a fiber. All measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation at 298(2) K using the Φ/ω scan technique.

The structures were solved by direct method and different Fourier syntheses using SHELXL-97 program, and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions with C–H distances of 0.93 Å and O–H distances of 0.82 Å riding on carrier atoms. Crystallographic data and experimental details of the structure determinations are listed in Table 1.

3. Results and discussion

3.1. IR Spectra

The IR spectra of these compounds have been recorded in the range of 4000–400 cm^{-1}. The IR spectroscopic data provide further support for the molecular constitution of these compounds. In majority of organoantimony(V) compounds the antimony has generally a coordination number of five. Because the vacant 5d orbital of antimony atom can accept lone electron pairs of ligands, in some cases the antimony may have a coordination number of six [8,15] or seven [31,12]. Whereas in compound **1**, the center of antimony atom is mainly considered as three center four electron bond using p-orbital of antimony rather than d-orbital contributing to describe the structure. The strong bands at

Table 1
Crystal data and structure refinement details for compounds **1**, **5**, **6**, **8**, **11** and **12**.

Compound	1	5	6	8	11	12
Empirical formula	$C_{28}H_{21}ClNO_2Sb$	$C_{65}H_{42}Cl_{12}O_9Sb_2$	$C_{31}H_{22}Cl_3O_2Sb$	$C_{28}H_{21}O_4S_2Sb$	$C_{32}H_{23}Br_2O_6Sb$	$C_{31}H_{24}BrO_3Sb$
Formula weight	560.66	1635.89	654.59	607.32	785.07	646.16
T (K)	298(2)	298(2)	298(2)	298(2)	298(2)	298(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Trigonal	Monoclinic
Space group	*P2(1)*	*P1̄*	*P2(1)/c*	*P1̄*	*P3(2)21*	*P2(1)/n*
a (Å)	9.1139(12)	9.2521(12)	16.3175(19)	9.0024(10)	17.4557(19)	13.5035(15)
b (Å)	9.5042(15)	16.616(2)	8.9520(9)	10.6491(17)	17.4557(19)	10.9498(12)
c (Å)	14.748(2)	25.279(3)	20.594(2)	14.4581(18)	10.9256(13)	18.867(3)
α (°)	90	73.8670(10)	90	68.674(2)	90	90
β (°)	107.026(2)	84.109(2)	112.450(2)	85.459(3)	90	106.923(2)
γ (°)	90	84.944(2)	90	86.171(3)	120	90
V (Å^3)	1221.5(3)	3706.2(8)	2780.3(5)	1286.0(3)	2883.0(6)	2668.9(5)
Z	2	2	4	2	3	4
$F(0\,0\,0)$	560	1620	1304	608	1152	1280
D_{cal} (g cm^{-3})	1.524	1.466	1.564	1.568	1.357	1.608
Crystal dimensions (mm)	0.40 × 0.18 × 0.13	0.38 × 0.36 × 0.23	0.48 × 0.28 × 0.12	0.56 × 0.52 × 0.27	0.50 × 0.15 × 0.12	0.52 × 0.45 × 0.41
θ range (°)	2.34–25.00	1.71–25.01	1.35–25.01	1.51–25.01	1.35–25.02	1.65–25.01
Reflections collected	5849	19 238	13 467	6654	10 800	12 921
Independent reflections	3872	12 740	4886	4450	3401	4688
R_{int}	0.0339	0.0486	0.0530	0.0291	0.0818	0.0582
Maximum and minimum transmission	0.8530 and 0.6319	0.7681 and 0.6561	0.8589 and 0.5725	0.7260 and 0.5371	0.7276 and 0.3319	0.4199 and 0.3493
Data/restraints/parameters	3872/1/298	12 740/2/799	4886/0/334	4450/2/317	3401/9/187	4688/0/325
Goodness-of-fit on F^2	1.489	0.969	1.025	0.958	0.975	1.000
Final R indices [$I > 2\sigma(I)$]	0.1188	0.0879	0.0395	0.0462	0.0456	0.0451
R indices (all date)	0.1308	0.1782	0.0638	0.0547	0.0599	0.0787
Largest difference in peak/hole [e A^{-3}]	8.270 and −1.417	0.947 and −0.856	1.185 and −0.517	0.983 and −2.071	0.548 and −0.507	0.796 and −0.994

about 1650–1640 cm^{-1} are attributed to the υC=N stretching vibration, which shift to lower frequency than free ligands (1680–1670 cm^{-1}). It is suggested that the coordination mode of 2-quinoline-carboxylate ligands with antimony ions is bidentate by nitrogen atom. In addition, it is worthy to note that besides the absorption at 1647 cm^{-1} belonging to C=N, there is another strong band at 593 cm^{-1} attribute to υSb–N in compound **1**, which is consistent with the crystal structure of compound **1**. In addition, the frequencies of Sb–C deformations appear between 465 and 435 cm^{-1} which is consistent with the literature [32]. In the IR spectra of compounds **1–12**, there is much common ground. Comparing with dissociative COOH ligands, absorption at 3250–3260 cm^{-1} disappears and absorption of Sb–O bond at 450–480 cm^{-1} appears. There are two strong absorption peaks attribute to phenyl of arylantimony in the IR spectra of compounds **1–12**, one is at 770–730 cm^{-1} and the other is at 710–690 cm^{-1}, which is just the characteristic absorption peaks of mono-substitution phenyl, however, absorption of phenyl of substitutional-benzo-carboxylates is complicated, however, it will shift to lower frequency than free ligands when the ligands take part in coordination to antimony atoms.

3.1.1. ^{1}H and ^{13}C NMR (CDCl$_3$)

In the ^{1}H NMR chemical shifts, the protons of Ar show a complicated multiplet between 6.82 and 9.24 ppm. All the protons in the compounds have been identified and the total number of protons calculated from the integration curve tallies with what is expected from the molecular formula. It is noted that most changes of the protons and ^{13}Cs on the macroring are to lowfield from shield by complexation [33,34]. The electronic structure on both the macroring and sidearm is perturbed by complexation but the macroring nuclei are more shielded while the sidearm nuclei are less shielded [33]. It is helpful in understanding the formation of weak H-bonds between a sidearm proton and an oxygen or other donor atoms on the macroring. Although the ^{1}H NMR chemical shifts of the protons of Ar are important, they are complicated multiplet. It is difficult to ascertain the protons of hydrogen-bonding interactions among carbon(Ar)–hydrogen–oxygen (or chlorine and so on). For O–H···O, it is evident that the chem-

ical shift at 4.24 ppm moves to lowfield in the ^{1}H NMR of compound **5**. In compound **5**, the protons of the methyl group at 2.31 ppm are assigned to solvent molecules methanol. In compounds **11** and **12**, the chemical shift at 9.12 or 9.08 is assigned to hydroxyl group of phenyl group. In the ^{13}C NMR chemical shifts, the nitrogen coordination of heterocyclic aprotic ligands to metal atoms is manifested in the form of deshielding of the C–4 carbon resonance by ∼3 ppm [35]. In compound **1**, the C–4 resonance of 2-quinoline-carboxylate is little affected about ∼3 ppm on coordination of the position for the free ligand suggesting a presence of Sb–N coordination (see the crystal structure of compound **1**). In addition, the signals for carbons of C=N bonds appear at about 154.2–158.7 ppm in compound **1**. Besides that, these derivatives also exhibit the expected signals due to the carbons of aryl groups at 120–155 ppm.

3.2. Crystal structure of compound **1**

The colorless crystals of compound **1** were obtained from CH$_2$Cl$_2$–petroleum ether. One of the approximate dimensions 0.40 × 0.18 × 0.13 mm was mounted in a glass capillary and used for data collection. Molecular conformation and atomic numbering schemes of compound **1** were illustrated in Fig. 1. The crystal structure of compound **1** can be reported as monomer. The most important feature in this structure is the very strong secondary interaction between antimony atom and the formally non-bonded nitrogen of the quinoline group. This is the very interaction which makes the coordination geometry of antimony to be converted from a trigonal-bipyramid to a distorted octahedron. In molecular structure of compound **1** (Fig. 1), the Sb atom is coordinated by the 2-quinoline-carboxylate ligand through an O atom and an imino N atom. The N=C bond distance [1.32(2) Å] in this compound is manifestations of the presence of a partial double bond, which suggests that the band Sb–N is a copulate band [36]. The distance of Sb–N [2.652(14) Å] is longer than that [2.259(4) Å and 2.249(4) Å] in reference [37]. There are hydrogen bonds in crystal structure of compound **1**. The selected bond lengths, angles and hydrogen bonds are listed in Tables 2 and 3, respectively. In Fig. 2, C–H···O hydrogen bonds link together adjacent molecules to one-dimension
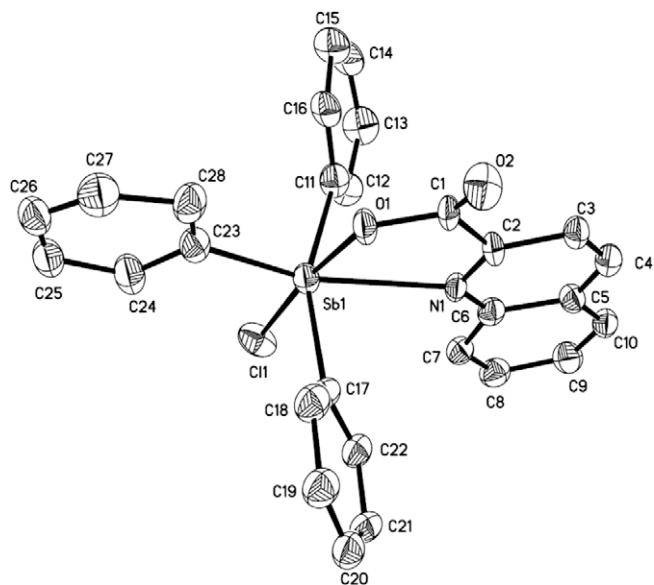
Fig. 1. The molecular structure of compound **1**.

Table 2
Selected bond lengths (Å) and angles (°) for compound **1**.

Sb(1)–O(1)	2.065(12)	Sb(1)–C(17)	2.127(16)
Sb(1)–N(1)	2.652(14)	Sb(1)–C(11)	2.166(16)
Sb(1)–Cl(1)	2.466(4)	Sb(1)–C(23)	2.13(2)
C(2)–N(1)	1.32(2)	N(1)–C(6)	1.32(2)
C(23)–Sb(1)–Cl(1)	99.1(5)	O(1)–Sb(1)–C(23)	87.1(6)
O(1)–Sb(1)–N(1)	71.6(4)	C(17)–Sb(1)–C(11)	156.3(6)
C(23)–Sb(1)–Cl(1)	99.1(5)	Cl(1)–Sb(1)–N(1)	102.3(3)
O(1)-Sb(1)-Cl(1)	173.3(4)		

Table 3
Hydrogen bonds (Å, °) for compound **1**.

D–H⋯A	d(H⋯A)	∠DHA	d(D⋯A)	Symmetry code
C4–H4⋯O2	2.50	140.5	3.27	1 − x, 0.5 + y, 2 − z
C15–H15⋯O2	2.64	124.6	3.26	1 − x, −0.5 + y, 2 − z

chain towards *b* axis. Furthermore, there are π⋯π and C–H⋯π interactions in the one-dimension chain, which make the structure is more stable. The distance of ii–iii (π⋯π) and ii–iv (π⋯π) is

3.721 Å and 4.196 Å, respectively, and the distance of H(26)-i (H⋯π) is 3.177 Å [i is the center of phenyl C(17)–C(22); ii is the center of phenyl C(23)–C(28); iii is the center of ring N(1)–C(6); iv is the center of ring C(5)–C(10)].

3.3. Crystal structure of compound **5**

A colorless crystal of compound **5** was obtained from CH_2Cl_2–petroleum ether solution. In the molecular structure of compound **5** with atom numbering scheme is depicted in Fig. 3. The selected bond distances and angles of the compound are listed in Table 4. As shown in Fig. 3, the asymmetric unit [2($C_{32}H_{19}Cl_6O_4Sb$)·CH_4O] contains two crystallographically independent molecules A and B, together with one methanol solvent molecules. Between the independent molecules, there are intermolecular hydrogen bonds C–H⋯O, which link them together. Conformations of the two independent molecules are almost the same, with only few differences in bond lengths and angles. The coordination about the Sb atom is slightly distorted from regular trigonal-bipyramidal geometry, with the equatorial plane occupied by three α-C from three phenyl groups and the axial positions shared by one coordinated oxygen atom from the ligand. The Sb–O distances [2.114(8), 2.145(8), 2.106(10), 2.130(10) Å] are within the literatures [38–41] but shorter than the sum of the van der Waals radii for Sb and O (3.2 Å) [42]. The angles of O(1)–Sb(1)–O(3) and O(5)–Sb(2)–O(7) are, respectively, 176.6(3)° and 176.0(3)°, showing quasi linear arrangement. The sum of the equatorial angles subtended at the Sb atoms is 360.0°. The Sb–C distances [2.094(13)–2.146(13) Å] are equal within experimental error and close to the single-bond value for trigonal-bipyramidal antimony. Similarly dimeric structures are formed through C–H⋯O hydrogen bonds between the independent molecules A and B in the asymmetric unit. Comparatively, two adjacent solvent molecules also form a similarly dimeric structure but through O–H⋯O hydrogen bonds (Fig. 4). The hydrogen bonds are listed in Table 5.

3.4. Crystal structure of compound **6**

A colorless crystal of compound **6** was obtained from CH_2Cl_2–petroleum ether solution. The molecular structures of compound **6** with the atom numbering scheme is depicted in Fig. 5. The selected bond distances and angles of the compound are listed in Table 6. The crystal structure of compound **6** can be reported as monomer. The antimony atom of the compound is five-coordinate, the coordination geometry of antimony can be described as a
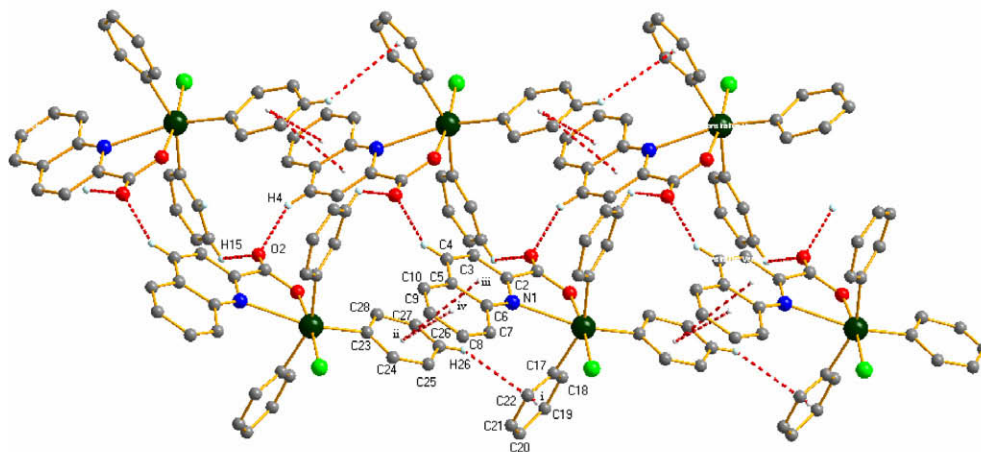

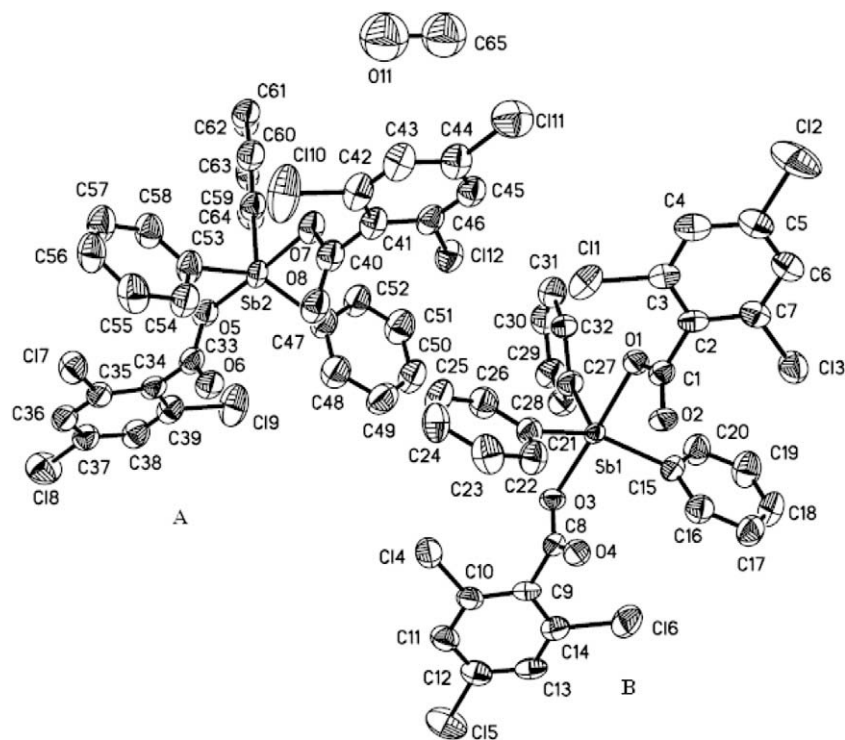**Fig. 2.** One-dimension chain of compound **1**.

Fig. 3. The molecular structure of compound **5**.

distorted trigonal-bipyramid. The three equatorial positions are occupied by the carbon atoms [C(14), C(20) and C(26)] of the three phenyl groups, while the atoms C(8) and O(1) occupy the axial positions. The apical Sb(1)–C(8) distance [2.174(4) Å] is slightly longer than the equatorial Sb(1)–C(14), Sb(1)–C(20) and Sb(1)–C(26) distances [2.127(4), 2.112(5) and 2.119(4) Å, respectively]. The Sb(1)–O(1) distance [2.305(3) Å] is longer than the corre-

sponding distance in Ph4SbOMe [2.061(7) Å] [43] and also longer than the typical Sb–O value [14]. A pair of weak C–H···Cl [C(16)···Cl(2) = 3.677(6) Å, H(16)···Cl(2) = 2.86 Å, C(16)–H(16)···Cl(2) = 147.0°] interactions generates similarly dimeric structures via crystallographic inversion centers (Fig. 6).

3.5. Crystal structure of compound **8**

A colorless crystal of compound **8** was obtained from CH_2Cl_2–petroleum ether solution. The molecular structure of compound **8** with the atom numbering scheme is depicted in Fig. 7. The se-

Table 4
Selected bond lengths (Å) and angles (°) for compound **5**.

Sb(1)–C(27)	2.094(13)	Sb(2)–C(53)	2.142(15)
Sb(1)–C(15)	2.107(12)	Sb(2)–O(5)	2.106(10)
Sb(1)–O(1)	2.114(8)	Sb(2)–C(59)	2.119(15)
Sb(1)–O(3)	2.145(8)	Sb(2)–O(7)	2.130(10)
Sb(1)–C(21)	2.146(13)	Sb(2)–C(47)	2.139(16)
C(27)–Sb(1)–C(15)	108.5(5)	C(59)–Sb(2)–C(47)	109.2(6)
C(15)–Sb(1)–C(21)	142.9(5)	C(59)–Sb(2)–C(53)	106.9(6)
O(1)–Sb(1)–O(3)	176.6(3)	C(47)–Sb(2)–C(53)	143.9(6)
C(27)–Sb(1)–C(21)	108.6(5)	O(5)–Sb(2)–O(7)	176.0(3)

Table 5
Hydrogen bonds (Å, °) for compound **5**.

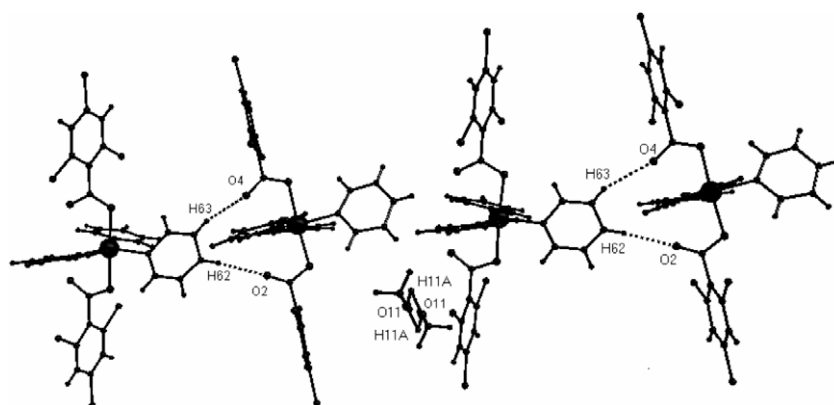| D–H···A	d(H···A)	<DHA	d(D···A)	Symmetry code
C63–H63···O4	2.71	137.7	3.459(19)	+x, 1 + y, +z
C62–H62···O2	2.50	168.7	3.416(19)	+x, 1 + y, +z
O11–H11a···O11	1.79	95.7	2.04(8)	1 − x,1 − y, 1 − z

Fig. 4. Similarly dimeric structures of compound **5**.
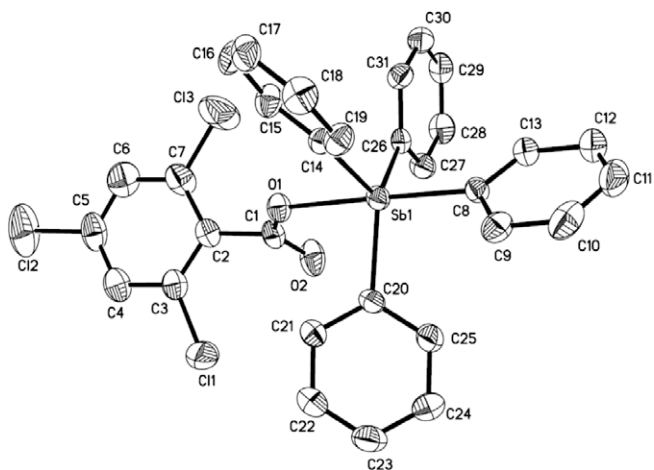
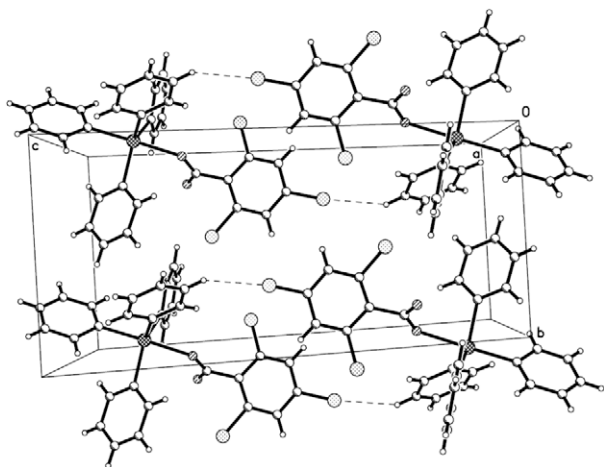**Fig. 5.** The molecular structure of compound **6**.

Fig. 6. Cell of compound **6**. In the crystal structure C–H···Cl hydrogen bonds link adjacent molecules into a dimmer [C16–H16···Cl2#1 0.93, 2.86, 3.677(6), 147.0, #1: −x + 1, −y, −z + 1].
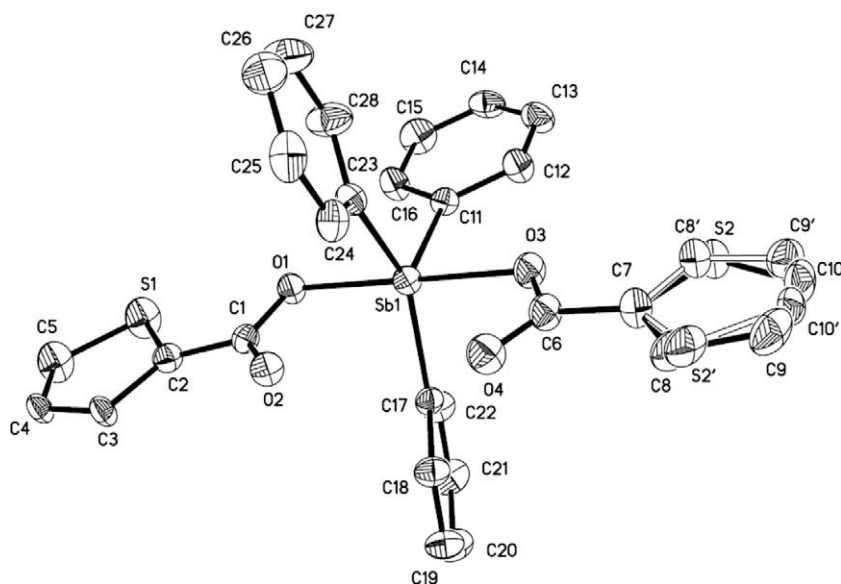
Table 6
Selected bond lengths (Å) and angles (°) for compound **6**.

Sb(1)–C(20)	2.112(5)	Sb(1)–O(1)	2.305(3)
Sb(1)–C(26)	2.119(4)	Sb(1)–C(8)	2.174(4)
Sb(1)–C(14)	2.127(4)	C(20)–Sb(1)–C(26)	131.36(17)
C(20)–Sb(1)–C(14)	115.12(17)	C(26)–Sb(1)–C(14)	110.29(18)
C(20)–Sb(1)–C(8)	94.72(18)	C(14)–Sb(1)–C(8)	98.63(17)
C(26)–Sb(1)–C(8)	94.92(17)	C(8)–Sb(1)–O(1)	178.76(15)

lected bond distances and angles of the compound are listed in Table 7. From Table 7, we can see that around Sb atom there are two short Sb–O bonds and a long one, indicating strong coordination and weak interaction. The distances of the long Sb–O bonds are much shorter than the sum of van der Waals radii of Sb and O atom, 3.2 Å [42] and are different from the corresponding distances in $Ph_3Sb(O_2C-2-C_4H_3S)_2$ [2.744(4), 2.949(4) Å] [24]. Obviously, there is apparent weak intramolecular Sb···O interaction in this compound. Therefore, the Sb atom could be described as three center four electron bond for the octahedron geometry. The central Sb1 atom is surrounded axially by O(1) and O(3) atoms and equatorially by C(11), C(17), C(23). The sum of equatorial angles is 359.84° which shows that these atoms are almost coplanar. Furthermore, the angle of axial place O(3)–Sb(1)–O(1) is 176.89(13)°, slightly deviating from 180°. In the crystal structure C–H···O [C(21)···O(4) = 3.610(8) Å, H(21)···O(4) = 2.68 Å, C(21)–H(21)···O(4) = 178.4°] hydrogen bonds link adjacent molecules to generate a one–dimensional chain along a axis (Fig. 8a) spreading towards b axis through C–H···π(C23–C28) ($d_{H10···\pi}$ = 2.60 Å) interaction to form a 2D network (Fig. 8b).

3.6. Crystal structure of compound **11**

A colorless crystal of compound **11** was obtained from CH_2Cl_2–petroleum ether solution. The molecular structures of compound **11** with the atom numbering scheme is depicted in Fig. 9. The selected bond distances and angles of the compound are listed in Table 8. The crystal structure of compound **11** can be reported as monomer lying on a 2-fold axis defined by the Sb atom and the ipso- and para-C atoms of one of the three antimony bound phenyl rings. The coordination environment of the Sb atom is trigonal-bipyramidal with the three phenyl substituents in the equatorial plane and the two monodentate benzoate ligands axial. The struc-
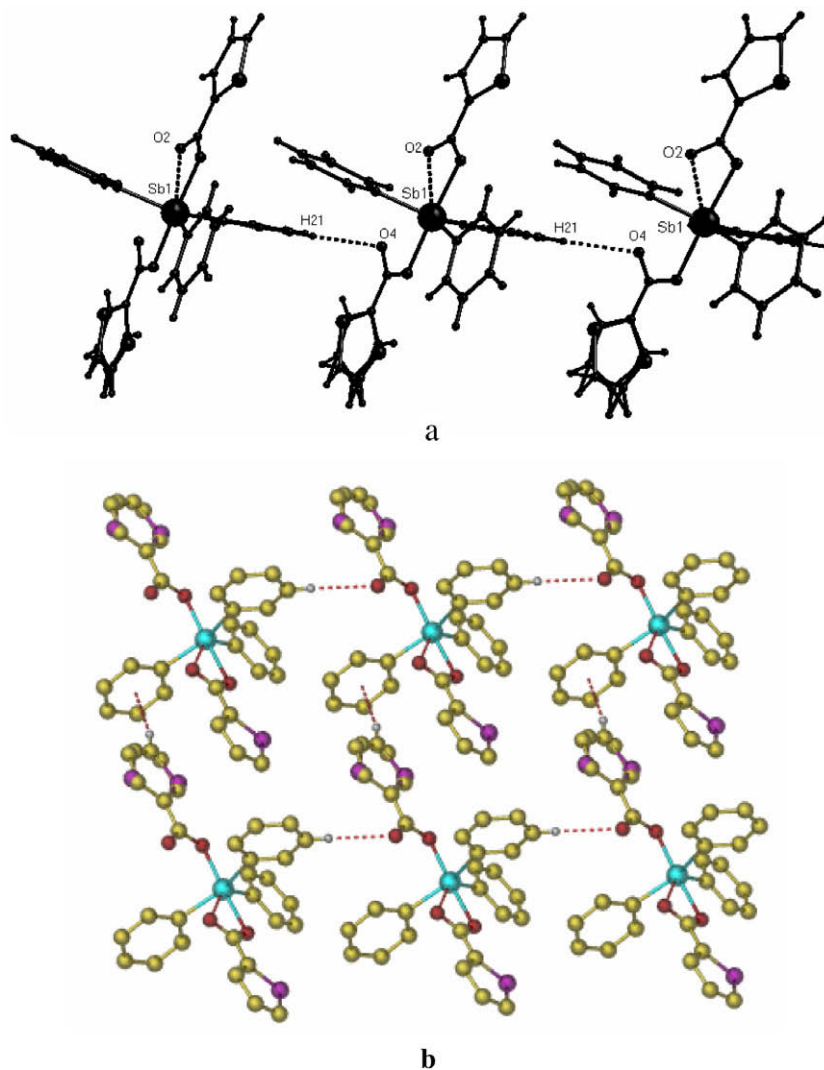

Fig. 7. The molecular structure of compound **8**.

Fig. 8. (a) A 1D chain of compound **8** and (b) a 2D network of compound **8**.

ture of compound **11** comprised isolated molecules with C2 molecular symmetry. The C2 axis was defined by the Sb(1)–C(14)–C(17) atoms. The coordination geometry around the antimony center is best described as a trigonal-bipyramid with two monodentate carboxylate ligands occupying the apical sites with an O(1)–Sb(1)–O(1a) angle 172.8(3)°. In the equatorial plane the angles C(8)–

Fig. 9. The molecular structure of compound **11**.

Sb(1)–C(8a) 134.1(4)°, C(8)–Sb(1)–C(14) 112.9(2)° and C(14)–Sb(1)–C(8a) 112.9(2)° depart significantly from 120° indicating some steric crowding in the molecule. The Sb(1)–O(1) bond distance 2.132(4) Å was longer than the corresponding distance 2.087(6) Å in $[4-(C_5H_5FeC_5H_4)C_6H_4COO]_2Sb(C_6H_4F-4)_3$ [44], but is rather shorter than the sum of van der Waals' radii of antimony and oxygen atom (2.2 and 1.4 Å, respectively) [42], as were the corresponding Sb–C distances 2.063(10)–2.130(6) Å compared to 2.123(9)–2.219(15) Å [38]. In the crystal structure C(15)–H(15)⋯Br(1) hydrogen bonds link adjacent molecules into one-dimensional chains (Fig. 10a) via crystallographic inversion centers. Among these chains, every six of them are linked into a channel by C11–H11⋯O1 hydrogen bonds. Simultaneously, these channels are linked together into a 3D alveolate structure (Fig. 10b) through C11–H11⋯O1 hydrogen bonds. Furthermore,
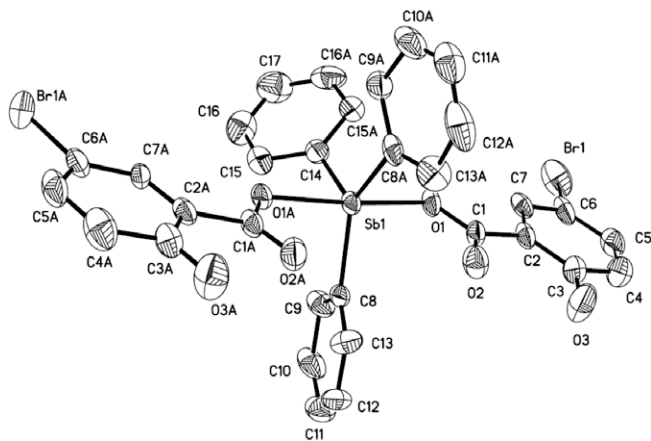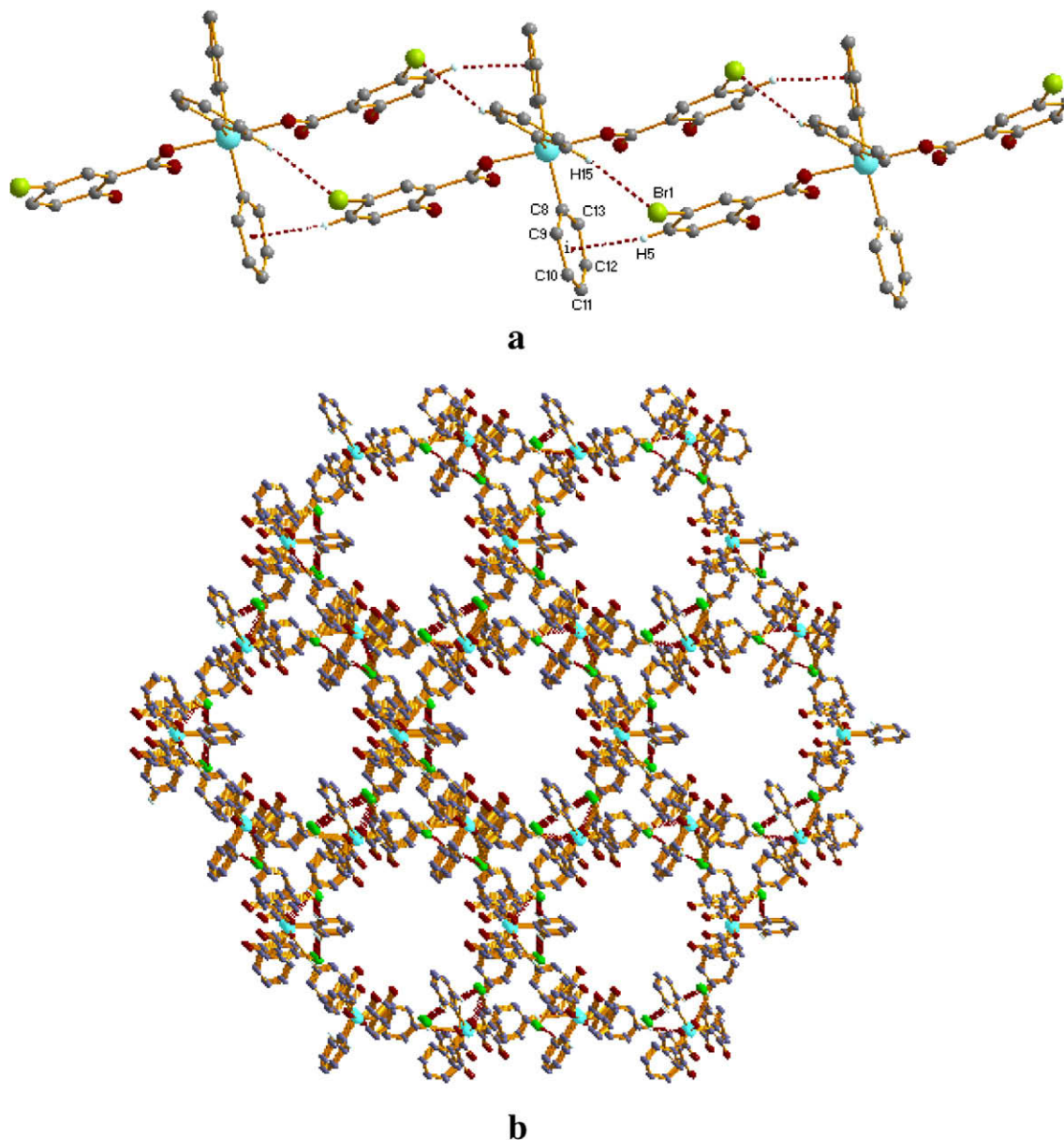
Table 7
Selected bond lengths (Å) and angles (°) for compound **8**.

Sb(1)–O(3)	2.109(4)	Sb(1)–O(2)	2.758(3)
Sb(1)–C(11)	2.128(5)	C(11)–Sb(1)–C(17)	109.46(18)
Sb(1)–C(17)	2.132(5)	C(11)–Sb(1)–C(23)	104.59(19)
Sb(1)–C(23)	2.139(5)	O(3)–Sb(1)–O(1)	176.89(13)
Sb(1)–O(1)	2.161(3)	C(17)–Sb(1)–C(23)	145.79(19)
Sb(1)–O(4)	2.970(4)		

Fig. 10. (a) One-dimensional chain of compound **11**; (b) 3D alveolate structure of compound **11** {C15–H15···Br1#1 and C15a–H15a···Br1#2 [0.93, 2.99, 3.823(8), 149.8] #1: x, y, $z − 1$ and #2: $x − y + 1$, $−y + 2$, $−z + 1/3$; C11–H11···O1#1 and C11A–H11A···O1#2 [0.93, 2.61, 3.532(10), 170.0] #1: $1 − y$, $1 + x − y$, $−0.333330 + z$ and #2: $1 − x$, $1 − x + y$, $0.66667 − z$}.

C–H···π interactions between H5s and phenyls (C8–C13) make the 3D network more stable (d_{H5-i} = 2.682 Å).

3.7. Crystal structure of compound **12**

A colorless crystal of compound **12** was obtained from CH_2Cl_2–petroleum ether solution. The molecular structures of

Table 8
Selected bond lengths (Å) and angles (°) for compound **11**.

Sb(1)–C(14)	2.063(10)	O(3)–H(3)	0.8200
Sb(1)–C(8)	2.130(6)	C(8)–Sb(1)–C(8)#1	134.1(4)
Sb(1)–O(1)	2.132(4)	C(8)–Sb(1)–O(1)#1	92.01(18)
Sb(1)–O(1)#1	2.132(4)	C(8)#1–Sb(1)–O(1)#1	90.80(19)
C(14)–Sb(1)–C(8)	112.9(2)	O(1)–Sb(1)–O(1)#1	172.8(3)
C(14)–Sb(1)–C(8)#1	112.9(2)		

Symmetry code: #1 $x − y + 1$, $−y + 2$, $−z + 1 − 3$.

compound **12** with the atom numbering scheme is depicted in Fig. 11. The selected bond distances and angles of the compound are listed in Table 9. This tretraphenylantimony derivative is synthesized by different method from Refs. [21,28], but the crystal structures are reported as similar monomers and the Sb atoms have the same distorted trigonalbipyramidal coordination with the O atoms of the carboxylate ligands in the axial positions while carbon atoms of the SbPh$_3$ unit occupy equatorial positions. In the crystal structure of compound **12**, in the axial position the angle C(26)–Sb(1)–O(1) is 175.44(14)°. The distance of Sb–O in compound **12** is slightly longer than that in tri-m-tolylantimony bis(benzenesulfonate), tri-p-tolylantimony bis(2,5-dimethylbenzenesulfonate) [21], tetraphenylantimony 2-furoinate and tetraphenylantimony benzoate [28]. Furthermore, the antimony–oxygen distance is different from Sb–O(H) 1.967(3) Å and Sb···O(P) 2.235(2) Å [44].

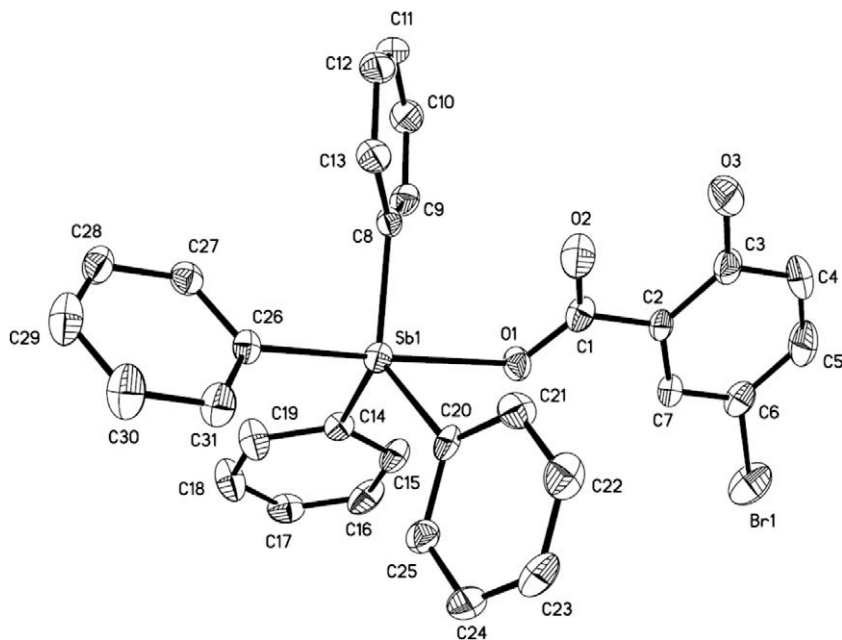**Fig. 11.** The molecular structure of compound **12**.

Table 9
Selected bond lengths (Å) and angles (°) for compound **12**.

Sb(1)–C(8)	2.107(5)	Sb(1)–O(1)	2.369(3)
Sb(1)–C(20)	2.110(5)	Sb(1)–C(14)	2.118(4)
Sb(1)–C(26)	2.167(5)	C(14)–Sb(1)–O(1)	84.42(16)
C(8)–Sb(1)–C(20)	130.45(19)	C(26)–Sb(1)–O(1)	175.44(14)
C(8)–Sb(1)–C(14)	112.89(19)	C(14)–Sb(1)–C(26)	100.10(17)
C(20)–Sb(1)–C(14)	111.93(19)	C(20)–Sb(1)–C(26)	97.23(19)
C(8)–Sb(1)–C(26)	94.78(19)		

Supplementary material

CCDC 679197, 731491, 731490, 731489, 731488 and 731487 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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