Novel Trinuclear Organoantimony Compounds

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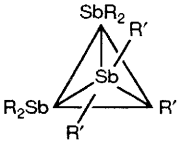
Novel trinuclear organoantimony compounds containing two Sb–Sb bonds have been synthesised and characterised.

There are a number of reports on organodistibines Sb_2R_4 and monocyclic organostibanes $(RSb)_n$ containing three-, four-, five- and six-membered rings.[1–3] However, there is apparently no report on organoantimony compounds containing open chains of Sb–Sb–Sb bonds. In this communication we report novel organoantimony compounds containing two Sb–Sb bonds and in which one antimony atom is in a different oxidation state compared to the other two.

The compounds were synthesised by the reaction of $LiSbR_2$ (R = Ph or tolyl) with R'_3SbBr_2 (R′ = Ph, tolyl or Me) in the molar ratio of 2:1 in a tetrahydrofuran (THF)–benzene mixture and were carried out in a nitrogen (oxygen free) atmosphere. The products are yellow microcrystalline moisture- and air-sensitive solids soluble in THF and benzene and moderately soluble in dichloromethane and chloroform. They have been characterised by elemental analyses, molecular



R = Ph or tolyl
R′ = Ph, tolyl or Me

weight- determination, UV-VIS, IR and far-IR, ^1H and ^{13}C NMR spectral studies.†

On the basis of elemental analyses these compounds can be formulated as $R'_3R_4Sb_3$. Vapour pressure osmometry measurement confirms the above formulation and shows that these are monomeric in benzene. Thermogravimetric analysis of these compounds has also been carried out in a nitrogen atmosphere in the range of room temperature to 540 °C. The end product in each case is antimony which corresponds to the percentage of antimony present in the compounds.[4]

In the far-IR spectra of these compounds a strong peak appears at 170–185 cm^{-1} which is attributable to the Sb–Sb bond. UV–VIS spectra of these tristibines were recorded both in the solid phase as DRS (diffuse reflectance spectra) and in ethanolic solution as absorption spectra. A single maximum around 315–330 nm was observed for these tristibines and there is no appreciable difference between the solid state and the solution spectra. This observation indicates that these tristibines are non-thermochromic, since marked differences between the solid state and solution spectra have been observed for all the thermochromic distibines.[5] The NMR spectra show the correct integration ratio of phenyl and methyl or tolyl protons in these compounds. In the NMR spectrum of $(tolyl)_3Sb–(SbPh_2)_2$, in C_6D_6, two peaks at δ 1.98 and 2.05 in the ratio of 2 : 1 are observed for methyl protons of the tolyl groups, showing that the two tolyl groups are in a different environment than the third one. Similarly two peaks were observed for the methyl protons at δ 1.37 and 1.39 in $Me_3Sb(SbPh_2)_2$. In the spectrum of $Ph_3Sb[Sb(Tolyl_2)]_2$ there is only one peak at δ 2.27 owing to the methyl protons of the tolyl groups showing that the tolyl groups are in same environment. The ^{13}C NMR spectra also confirm the above conclusion regarding the different environments of methyl and tolyl protons in the respective tristibines.

On the basis of the observed geometry of most of the five coordinated antimony compounds being trigonal bipyramid, it is suggested that these tristibines also have a trigonal bipyramid structure. Although we are trying to obtain good quality crystals for X-ray crystallography, on the basis of the NMR data it is clear that in these compounds the two SbR_2 groups are in equatorial positions whereas one of the three R′ groups occupies an equatorial position and the other two occupy the axial positions.

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† *Selected data* for $(Tolyl)_3Sb–(SbPh_2)_2$: M = 903 (944); UV-VIS: solution (solid) 315 nm (325 nm); far-IR (v/cm^{-1}): 175(m), 181(m), 490(s), 460(m); ^1H NMR (C_6D_6): δ 1.98 (s, 6H), 2.05 (s, 3H), 7.04–7.81 (m, aromatic 32H); ^{13}C NMR (CD_3OD): δ 27.43, 29.25, 144.32–157.84 (aromatic carbon).

$Ph_3Sb–[Sb(Tolyl)_2]_2$: M = 908 (958); UV-VIS: solution (solid) 322 nm (340 nm); far-IR (v/cm^{-1}): 178(m), 168(m), 490(s); ^1H NMR (C_6D_6): δ 2.27 (s, 12H), 7.15–7.94 (m, aromatic 31H); ^{13}C NMR (CD_3OD): δ 27.33, 140.44–151.34 (aromatic carbon).

$Me_3Sb–[Sb(Tolyl)_2]_2$: M = 738 (772); far-IR (v/cm^{-1}): 160(m), 178(s), 560, 492(w); ^1H NMR (C_6D_6): δ 1.25 (s, 6H), 1.32 (s, 3H), 2.23 (s, 12H), 6.83–7.38 (m, aromatic 16H).

$Me_3Sb–(SbPh_2)_2$: ^1H NMR (C_6D_6): 1.37 (s, 6H), 1.39 (s, 3H), 6.95–7.29 (m, aromatic 20H).