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DODECAFLUORO- AND DODECACHLORO-5,10-*o*-BENZENOSTIBANTHRENE

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Summary

$Sb_2(C_6F_4)_3$ and $Sb_2(C_6Cl_4)_3$ can be synthesised simply by heating together 1,2-$I_2C_6X_4$ (X = F, Cl) and powdered antimony in sealed tubes. Both compounds form hemi-solvates with a variety of organic solvents; typically, the weak hexane solvate of $Sb_2(C_6F_4)_3$ loses hexane slowly at room temperature. The mass spectra, and the ^{13}C NMR spectrum of $Sb_2(C_6F_4)_3$, are described. Chlorine reacts with $Sb_2(C_6F_4)_3$ to give $Sb_2(C_6F_4)_3Cl_4$ which, on boiling with water, forms the oxide $Sb_2(C_6F_4)_3O_2$. $Sb_2(C_6F_4)_3$ is oxidised by concentrated nitric acid to the dinitrate $Sb_2(C_6F_4)_3(OH)_2(NO_3)_2$ which slowly hydrolyses in aqueous solution to form the tetrahydroxo derivative $Sb_2(C_6F_4)_3(OH)_4$.

Introduction

Glistening crystals of dodecafluoro-5,10-*o*-benzenostibanthrene [1] (perfluoro-distibatriptycene, I) grown for X-ray work from hexane slowly lost their bright, transparent appearance and changed to white, opaque lumps on standing in the air at room temperature. This behaviour suggested that a metastable crystalline phase might have been formed; however, on placing the crystals in a mass spectrometer and slowly warming up the insertion probe it was found that hexane ($m/e = 86$) was evolved. After pumping away the hexane and heating the probe further the normal mass spectrum of $Sb_2(C_6F_4)_3$ was observed. Obviously, though unexpectedly, a solvate had been formed with the hexane. The analytical samples described in our previous communication [1] had been heated to about 150 °C in a vacuum (ca. 10^{-4} mmHg) before study and had lost all adhering solvent in the process. The nature of this and similar solvates and the chemistry of $Sb_2(C_6F_4)_3$ and its chloro-analogue $Sb_2(C_6Cl_4)_3$ have been investigated with the results described below.

Results and discussion

Elemental analysis of crystals grown from hexane and air-dried at room temperature demonstrated the presence of half a mole of solvent per mole of $Sb_2(C_6F_4)_3$.

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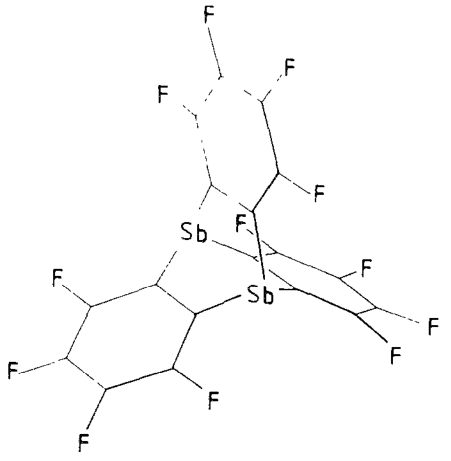
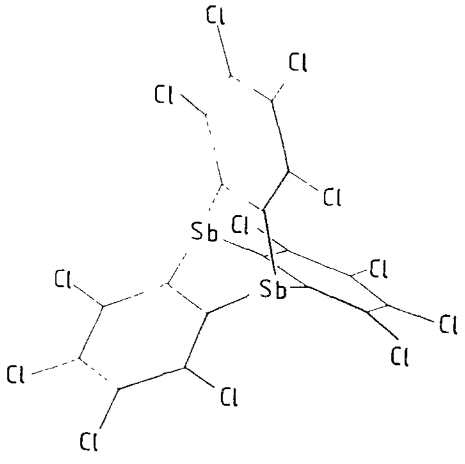


(I)



(II)

Thermogravimetric analysis showed that the hexane was held only weakly and began to come off quite rapidly only a few degrees above room temperature. Crystals of solvate which had been pumped dry under vacuum at room temperature for 5 min and stored in a stoppered bottle for a week showed a 4.0% weight loss on heating due to evolution of hexane (the calculated weight loss for a solvate of composition $Sb_2(C_6F_4)_3 \cdot 0.5$hexane is 5.90%). A more accurate determination of the weight loss at a constant 70 °C for crystals taken from the mother liquor and air-dried to constant weight at room temperature, showed that all the hexane was lost within 2.5 h (5.87% weight loss). Even at room temperature the hexane solvate effloresced losing 2.5% of the hexane in 24 h, 67% in eight days and 96% after two weeks. The C–H stretching frequencies in the solvate occurred at 2955, 2921, 2865 and 2850sh cm^{-1} which are virtually identical in position to those recorded for a dilute solution of hexane in hexachlorobutadiene; very minor variations in the relative peak heights were apparent, in particular, the shoulder at 2850 cm^{-1} in the solvate becomes slightly more intense and forms a doublet with the peak at 2865 cm^{-1} in the hexane spectrum. The instability of this solvate, and the infrared data, suggest that the hexane is simply trapped in the crystal lattice and has essentially no chemical interaction with the $Sb_2(C_6F_4)_3$ molecules.

Cyclohexane, toluene and benzene similarly form hemi-solvates with $Sb_2(C_6F_4)_3$ which appear to be slightly more stable than that formed by hexane; the benzene solvate lost solvent least readily and even after 5 days at 70 °C suffered only 90% dissociation. Chloroform and acetone do not form solvates that are stable at room temperature.

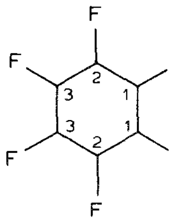
Since there has been some dispute between ourselves [1] and Cullen and Wu [2] over the true identity of $Sb_2(C_6F_4)_3$ we attempted to prepare the chloro-analogue via "direct synthesis", by simply heating 1,2-diiodotetrachlorobenzene with an excess of antimony powder. This method was chosen because the necessary lithium reagent, 1,2-$Li_2C_6Cl_4$, required for a more conventional synthesis has not yet been made and, furthermore, $P_2(C_6H_4)_3$ [3], $As_2(C_6H_4)_3$ [4] and $Sb_2(C_6F_4)_3$ [4] have all been prepared by the direct route. Dodecachloro-5,10-*o*-benzenostibanthrene proved to be very insoluble in most organic solvents and had to be extracted from the reaction mixture using several aliquots of boiling dimethylformamide or boiling nitrobenzene; virtually all the SbI_3 co-product was soluble in the first aliquot which could then be discarded. As with $Sb_2(C_6F_4)_3$, hemi-solvates were formed when $Sb_2(C_6Cl_4)_3$ crystallized out on cooling from dimethylformamide, diethylformamide, pyridine and nitrobenzene; the solvents can be removed by heating the solvates above 120 °C in vacuum.

Close examination of a typical cold reaction tube revealed the presence of a few large, colourless crystals mixed with the antimony triiodide at what had been the cooler end of the tube when it had been in the oven. These crystals proved to be hygroscopic, they attacked caesium iodide infrared plates producing a red-orange deposit of antimony triiodide and gave a positive test for chloride on being dissolved in water; typical reactions of antimony trichloride. Obviously attack of the chloro-aromatic groups is occurring during the heating process helping to explain both the relatively low yields of $Sb_2(C_6Cl_4)_3$ (ca. 5%) and the carbon-like appearance of the insoluble residues mixed with the excess of elemental antimony.

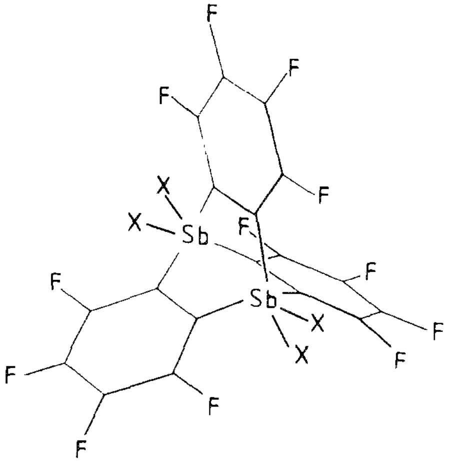
Due to the analytical difficulties mentioned in the Experimental section, the early attempts to identify $Sb_2(C_6F_4)_3$ relied heavily on mass spectrometry. The parent ion shows a relatively intense (ca. 40%) group of peaks around 688 mu and the base peak in the spectrum is due to $SbC_6F_4^+$. Unlike the closely related compounds $NP(C_6H_4)_3$ [5] and $P_2(C_6H_4)_3$ [3], which appear to be particularly robust towards electron impact and show doubly-charged and triply-charged parent ions, $Sb_2(C_6F_4)_3$ has no multiply-charged ions in its mass spectrum. The polyphenylene ions $(C_6F_4)_3^+$ and $(C_6F_4)_2^+$ together with their fragmentation products are responsible for much of the lower-intensity background peaks. Antimony-containing fragment ions giving peaks visible at low gain were $SbC_{18}F_{10}^+$ (i.e. P-SbF_2), $Sb(C_6F_4)_2^+$, $SbC_6F_4^+$, SbF_2^+, SbF^+ and Sb^+. Although $Sb_2(C_6F_4)_3$ is less robust towards electron impact than $P_2(C_6H_4)_3$ and $NP(C_6H_4)_3$ it is still a very stable molecule resisting attack by water at 300 °C and iodine in refluxing chloroform; thermal decomposition occurs only slowly at 400 °C in a vacuum and sublimation takes place rapidly in the open air above 160 °C.

The chloro-analogue, $Sb_2(C_6Cl_4)_3$ (II), has a much richer mass spectrum with $SbC_6X_4^+$ ions again responsible for the base peak. Although the parent ion has a high relative intensity (ca. 50%) no doubly-charged molecular ion could be detected; important antimony-containing species were $Sb_2C_{18}Cl_{10}^+$, $SbC_{18}Cl_{11}^+$, $SbC_{18}Cl_{10}^+$, $SbC_{18}Cl_9^+$, $SbC_{12}Cl_{10}^+$, $SbC_{12}Cl_8^+$, $SbC_{12}Cl_6^+$, $SbC_6Cl_6^+$, $SbC_6Cl_4^+$, $SbC_6Cl_2^+$, $SbCl_2^+$ and $SbCl^+$. The occurrence of several chlorine-migration reactions is evident by the observation of "chlorine-rich" ions such as $C_{12}Cl_{10}^+$, $C_6Cl_6^+$, $C_6Cl_5^+$, $SbC_6Cl_6^+$, $SbCl_2^+$ and $SbCl^+$.

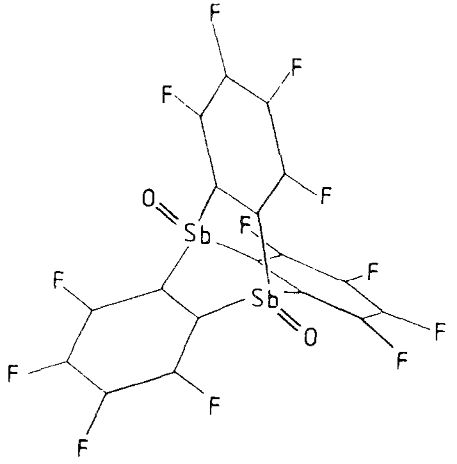
The ^{13}C NMR spectrum of $Sb_2(C_6F_4)_3$ dissolved in acetone-d_6 is obviously of second order but shows the expected three groups of peaks corresponding to the three types of carbon present in the molecule. The group at 130.2 ppm (relative to tetramethylsilane) is identical in shape to that at 91.9 ppm in the spectrum of 1,2-diiodotetrafluorobenzene; as the chemical shift of this group is particularly sensitive to the substituent in the 1,2-positions it is assigned to C(1) carbon atoms. The other two resonances, due to C(3) and C(2) carbon atoms, are centred at 140.8 and 151.1 ppm and show a doublet splitting of 244 and 235 Hz, respectively. The corresponding shifts for C(3) and C(2) carbon atoms in 1,2-$I_2C_6F_4$ and 1,2-$Br_2C_6F_4$ are 140.5, 140.7 and 148.5, 146.3 ppm, respectively.



Although $Sb_2(C_6F_4)_3$ does not react with iodine in refluxing chloroform, chlorine causes oxidation and produces a precipitate of $Sb_2(C_6F_4)_3Cl_4$ (III) within a few seconds at room temperature in carbon tetrachloride. The chloride does not appear to hydrolyse to any appreciable extent in air at room temperature but it does absorb two molecules of water quite readily to form a dihydrate. Although no parent ion, $Sb_2(C_6F_4)_3Cl_4^+$, could be detected in the mass spectrum other chloro-ions $Sb_2(C_6F_4)_3Cl_3^+$, $Sb_2(C_6F_4)_3Cl_2^+$ and $Sb_2(C_6F_4)_3Cl^+$ gave readily identifiable peaks with about 22, 25 and 95% intensities relative to the base peak at *m/e* 269 due to $SbC_6F_4^+$. Thermal decomposition in a vacuum gave a complex mixture of products which included $Sb_2(C_6F_4)_3$ together with unidentified carbon-chlorine and biphenyl species.



(III, X = Cl;
V, X = OH)



(IV)

On boiling with a large excess of distilled water $Sb_2(C_6F_4)_3\,Cl_4$ was hydrolysed to give a water-insoluble solid which analysed as the dioxide $Sb_2(C_6F_4)_3O_2$. In view of Chremos and Zingaro's work [6] it seems unlikely that this is the simple compound shown in IV and it may be, at least partially, polymeric. The large number of infrared bands in the spectrum of $Sb_2(C_6F_4)_3O_2$ also suggests a molecule with a more complex structure than that with the relatively high symmetry of IV. Attempts to obtain a molecular weight mass spectrometrically were foiled because of a ready thermal decomposition which occurs before the oxide begins to volatilize; the major product of this decomposition was shown by infrared and mass spectroscopy to be $Sb_2(C_6F_4)_3$. Compounds having identical infrared spectra to $Sb_2(C_6F_4)_3O_2$ were obtained both by the prolonged oxidation by hydrogen peroxide of $Sb_2(C_6F_4)_3$

dissolved in acetone, and by hydrolysis of the ill-defined solid produced when bromine attacks $Sb_2(C_6F_4)_3$ in carbon tetrachloride.

Hot, concentrated nitric acid readily dissolves $Sb_2(C_6F_4)_3$. On cooling and dilution with distilled water it was found that nothing could be extracted from the solution by diethyl ether. However, on standing for two days the solution deposited colourless, needle-like crystals of what is probably the dinitrate, $Sb_2(C_6F_4)_3(OH)_2(NO_3)_2$. During attempts to recrystallize the nitrate from water it was noticed that tiny bubbles of gas (oxygen?) formed in the solutions on standing and that the amount of "nitrogen" in the recrystallized samples fell with each successive crystallization being virtually zero after four recrystallizations; the compound then analysed as the tetrahydroxo compound $Sb_2(C_6F_4)_3(OH)_4$ (V). Obviously the nitrate is hydrolytically unstable even at room temperature. The infrared spectrum of V is virtually identical to that of the oxide $Sb_2(C_6F_4)_3O_2$ except for a slight change in the position of the broad "Sb–O" band at 624 cm^{-1} (which is at about 640 cm^{-1} in the oxide). The analysis would, of course, fit the formula for the dihydrate of the oxide, $Sb_2(C_6F_4)_3O_2(H_2O)_2$; however, as the oxide is not soluble in water even on boiling whereas V is freely soluble in tepid water it is highly unlikely that V is simply a hydrate of the oxide. Certainly no bands for coordinated water could be seen in the infrared spectrum of V and no water was lost on heating to 200 °C in air.

Experimental

The sealed-tube syntheses were carried out in evacuated Pyrex glass tubes which had been thoroughly baked out under vacuum using a free flame. Quoted analyses were carried out by Dornis and Kolbe, 4330 Mülheim/Ruhr and by the Micro-analytical Laboratory, Manchester University.

Preparation of $Sb_2(C_6F_4)_3$

Approximately 1 g samples of powdered antimony and 1,2-diiodotetrafluorobenzene were heated together in a sealed tube at 250 °C overnight. The tube was cut open and the solid product crushed to a powder before being extracted with 4 × 25 cm^3 aliquots of 60–80 °C petroleum ether in which the co-product SbI_3 is practically insoluble. The slight yellow or pink colours sometimes observed in the extracts can be removed by boiling with charcoal; the yield of recrystallized product is about 60% based on $C_6F_4I_2$. An analytical sample was obtained by heating the crystals from petroleum ether to 140 °C in a vacuum to drive off the trapped solvent, m.p. 258–259 °C (Found: C, 31.1, 31.4; H, 0.0, 0.0; F, 33.8, 33.0. $C_{18}F_{12}Sb_2$ calcd.: C, 31.4; H, 0.0; F, 33.2%). A small quantity of product was lost by sublimation during the drying procedure which lasted for 10–20 min.

If the sample of $Sb_2(C_6F_4)_3$ is recrystallized from hexane and air-dried at room temperature the following typical analytical figures are obtained: Found: C, 33.9, 34.1; H, 0.9, 0.9; F, 25.3, 25.4. $C_{18}F_{12}Sb \cdot 0.5$hexane calcd.: C, 34.5; H, 1.0; F, 31.2%. These samples still melted at 258–259 °C presumably because the hexane was driven off at some lower temperature and the recorded m.p. was that of unsolvated $Sb_2(C_6F_4)_3$. The low fluorine figures quoted above typify the extreme problems several different microanalysts had in obtaining meaningful data for this compound unless great care was taken; apparently this stems from the simultaneous presence of both fluorine and antimony. Sharp melting points and identical mass spectra for the various samples show that it is unlikely the descrepancies in analysis arose from impure samples. As much as 1.5% "nitrogen" was quoted in some analytical results even though no nitrogen-containing compounds had been in contact with the $Sb_2(C_6F_4)_3$ samples; the "nitrogen" reported is probably silicon tetrafluoride formed by attack of the compound on the silica combustion tube used in the analysis. Infrared spectrum (cm^{-1}) of $Sb_2(C_6F_4)_3$: 1610w, 1584m, 1431vs, 1325w, 1306w, 1281m, 1256m, 1091s, 1047w, 1013s, 808m, 754m, 708w, 640w, 467w, 361m, 348sh. The infrared spectrum of the hexane solvate is essentially identical to that of solvent-free $Sb_2(C_6F_4)_3$ except for the C–H stretching frequencies quoted in the Discussion and a splitting of the 1091 cm^{-1} peak into a doublet (1091, 1085 cm^{-1})

Loss of hexane from $Sb_2(C_6F_4)_3 \cdot 0.5(C_6H_{14})$

The solvate (110.988 mg) was heated in an open tube to 70 °C and the weight loss measured after varying times: 5.121 mg loss in 0.5 h (4.61%), 6.482 mg loss in 1 h (5.84%), 6.520 mg loss in 2.5 h (5.87%) and 6.519 mg loss in 24 h (5.87%). The calculated loss for removal of all the hexane from $Sb_2(C_6F_4)_3 \cdot 0.5(C_6H_{14})$ is 5.90%. The temperature of 70 °C was chosen for heating because samples of $Sb_2(C_6F_4)_3$ showed long-term weight stability whereas at 100 °C slow sublimation out of the weighing bottles occurred to the extent of about 200 μg per day.

Hexane is slowly lost from the solvate on standing at room temperature. A 95.691 mg sample left in an open tube at 17–20 °C lost 0.387 mg of hexane after 2 d (6.8% dissociation), 3.777 mg after 8 d (66.9%), 5.413 mg after 2 weeks (95.9%) and 5.533 mg after six weeks (98.0%)

Formation of a cyclohexane solvate of $Sb_2(C_6F_4)_3$

Crystallization of a hot solution of $Sb_2(C_6F_4)_3$ in cyclohexane produced a crop of tiny crystals which lost their lustre and collapsed to a powdery solid on heating to 70 °C in an oven. On monitoring the weight loss which occurred it was apparent that the cyclohexane solvate lost solvent more slowly than the n-hexane solvate described above. A sample of 49.178 mg lost 0.232 mg after 0.5 h at 70 °C (0.47% loss), 0.664 mg after 1.5 h (1.35%) and 2.859 mg after 17 h (5.81%). Calculated loss for removal of all the cyclohexane from $Sb_2(C_6F_4)_3 \cdot 0.5$ (cyclohexane) is 5.76%. Analysis confirmed the presence of half a mole of cyclohexane in the solvate (Found: C, 34.5; H, 0.8; F, 31.2. $C_{21}H_6F_{12}Sb_2$ calcd.: C, 34.6; H, 0.8; F, 31.2%).

Attempted formation of a chloroform solvate of $Sb_2(C_6F_4)_3$

$Sb_2(C_6F_4)_3$ is very soluble in chloroform and the solvent had to be allowed to evaporate off completely at room temperature in order to isolate the solvate. A sample of solvate which had been allowed to stand overnight in the air to dry completely showed evidence of efflorescence in that the solid had become somewhat opaque instead of remaining as transparent crystals. On heating to 70 °C a weighed sample collapsed to a white powder as the remaining chloroform was driven off. Although the solid behaved as a solvate in initially forming crystalline material which became white and amorphous on heating, the weight loss (4.82%) was considerably less than the loss calculated for half a mole of chloroform (7.99%). If a solvate had been formed the descrepancy between the above figures must represent the extent of efflorescence which occurred during the overnight period whilst the solid was drying at room temperature. The solid which separated from acetone behaved in a similar manner to this chloroform solvate in not retaining stoichiometric quantities of solvent after drying overnight.

Formation of a toluene solvate of $Sb_2(C_6F_4)_3$

Very large crystals of solvate were formed when hot, concentrated solutions of $Sb_2(C_6F_4)_3$ in toluene were allowed to cool. After allowing the crystals to dry on a filter paper for half an hour in the open air, analysis showed the retention of half a mole of solvent (Found: C, 35.7; H, 0.7; F, 31.0. $C_{21 \cdot 5}H_4F_{12}Sb_2$ calcd.: C, 35.2; H, 0.5; F, 31.1%).

Formation of a benzene solvate of $Sb_2(C_6F_4)_3$

The crystals which separated from concentrated benzene solutions of $Sb_2(C_6F_4)_3$ held solvent relatively tenaciously on heating at 70 °C. A 176.259 mg sample lost 5.098 mg after 19 h (2.89%), 8.305 mg after 3 d (4.71%), 8.540 mg after 6 d (4.85%). The calculated loss for 0.5 mol of benzene is 5.37%. Elemental analysis of the solvate confirmed the presence of the hemi-solvate (Found: C, 34.0; H, 0.3; F, 29.6. $C_{21}H_3F_{12}Sb_2$ calcd.: C, 34.7; H, 0.4; F, 31.4%). The C–H stretching frequencies occurred at 3091, 3075 and 3035 cm^{-1} in the infrared spectrum, being essentially identical to those of benzene dissolved in hexachlorobutadiene.

Attempted reaction of $Sb_2(C_6F_4)_3$ with iodine

A chloroform solution of $Sb_2(C_6F_4)_3$ was refluxed with an excess of iodine for 2 h. Removal of the solvent gave only starting material as a white solid melting at 258 °C.

Attempted reaction of $Sb_2(C_6F_4)_3$ with methyl iodide

A mixture of $Sb_2(C_6F_4)_3$ and methyl iodide was refluxed for 2.5 h, after which time the solvent methyl iodide was removed and the remaining solid dried under vacuum, m.p. 258–259 °C. A portion of the solid was shaken with distilled water which was then tested with silver nitrate; no silver iodide was precipitated.

Attempts to make $Sb_2(C_6F_4)_2O$

1,2-Diiodotetrafluorobenzene was heated in a sealed tube at 250 °C with approximately equal amounts of antimony powder and Sb_2O_3. After cooling and opening the tube, the contents were extracted with boiling 60–80 °C petroleum ether and the solution clarified with charcoal. The resulting crystals, which melted at 257–258 °C, were of $Sb_2(C_6F_4)_3$; a minor second crop of crystals melted, before recrystallization, at 255 °C. Thus no $Sb_2(C_6F_4)_2O$ has been formed under similar conditions to those which produced $As_2(C_6F_4)_2O$ [7]. Furthermore, it is obvious that $Sb_2(C_6F_4)_3$ does not react with Sb_2O_3.

Approximately 0.5 g of $Sb_2(C_6F_4)_3$ were heated with two drops of distilled water in a sealed, evacuated tube; there was no apparent reaction after 5 h at 250 °C. After 18 h at 300 °C the tube was opened and the solid remaining crystallized from petroleum ether, m.p. 257–258 °C; before purification the melting point was 254–257 °C. Hence there is no reaction with water under these conditions; in contrast, $Sb(C_6F_5)_3$ slowly loses C_6F_5 groups on contact with water at room temperature [8].

Oxidation of approximately 1 g of $Sb_2(C_6F_4)_3$ with 5 g potassium dichromate, 12

cm^3 water, 5 cm^3 conc. sulphuric acid and 12 cm^3 of glacial acetic acid gave only one or two crystals of impure starting material on neutralizing the mixture with sodium bicarbonate and extracting with diethyl ether.

Reaction of antimony with mercuric tetrafluorophthalate

It was shown previously [1] that $Sb_2(C_6F_4)_3$ can be made by heating together antimony powder and $(C_6F_4Hg)_3$. As the latter mercurial is prepared by thermal decarboxylation of mercuric tetrafluorophthalate it appeared reasonable to attempt the synthesis of $Sb_2(C_6F_4)_3$ directly from a mixture of Sb and $Hg(OOC)_2C_6F_4$ heated on a vacuum line. Extraction of the residues with 60–80 °C petroleum ether gave a small quantity (ca. 5%) of $Sb_2(C_6F_4)_3$ solvate identified by comparison of its infrared spectrum with that of an authentic sample.

Reaction of $Sb_2(C_6F_4)_3$ with chlorine

When chlorine was passed into a carbon tetrachloride solution of $Sb_2(C_6F_4)_3$ the solution suddenly became turbid after a few seconds at room temperature and began to precipitate a white solid. After 5 min the chlorine cylinder was closed and the solid collected, after washing with copious amounts of carbon tetrachloride. The analytical sample was recrystallized from an un-dried $CCl_4/CHCl_3$ mixture by cooling in a refrigerator for two weeks (Found: C, 24.9, 25.0, 25.0; H, 0.1, 0.4, 0.3; Cl, 16.5; F, 25.2, 25.9, 25.8. $Sb_2C_{18}F_{12}H_4O_2Cl_4$ calcd.: C, 25.0; H, 0.5; Cl, 16.4; F, 26.3%). The unhydrated compound has a very sharp melting-decomposition point of 184 °C and is very soluble in ether, alcohol, chloroform and toluene; it is sparingly soluble in 60–80 °C petroleum ether and carbon tetrachloride. Infrared spectrum of $Sb_2(C_6F_4)_3Cl_4$ (cm^{-1}): 1610w b, 1587w b, 1484s, 1320w, 1305w, 1294w, 1240m, 1231sh, 1109s, 1024s 816m, 775m b, 758m, 706m sharp, 639m, 467w, 423w, 370m, 324m, 296m. When the chloride is in contact with damp solvents a peak begins to develop at 3515 cm^{-1}.

Reaction of $Sb_2(C_6F_4)_3Cl_4$ with water

A sample of $Sb_2(C_6F_4)_3Cl_4$ was hydrolysed by boiling with three aliquots of distilled water, each aliquot of excess water being decanted from the insoluble solid before more water was added. The isolated solid $Sb_2(C_6F_4)_3O_2$, which was dried overnight at 70 °C, had a rather poorly defined melting-decomposition point of about 336 °C; a sublimate of needle crystals ($Sb_2(C_6F_4)_3$?) was evident in the melting point tube some 20 °C below the melting point (Found: C, 29.3, 29.3; H, 0.1, 0.1; F, 31.7. $Sb_2C_{18}F_{12}O_2$ calcd.: C, 30.0; H, 0.0; F, 31.7%). When heated in a vacuum the oxide gave a white sublimate which the infrared and mass spectra showed was pure $Sb_2(C_6F_4)_3$. On being heated on a mass spectral probe the oxide gave no spectrum up to 250 °C at which point the spectrum of $Sb_2(C_6F_4)_3$ began to appear.

Infrared spectrum of $Sb_2(C_6F_4)_3O_2$ (cm^{-1}): 1596mb, 1327w, 1308w, 1296w sh, 1290w, 1261w, 1245m, 1235m, 1130w, 1113, 1107 doublet s, 1047w, 1032s sh, 1026s, 832vw, 812w, 799w, 765w, 640s b, 595w, 576w, 544mb, 513w, 469w, 372m, 365msh, 305w, 277m, 270msh.

Reaction of $Sb_2(C_6F_4)_3$ with nitric acid

$Sb_2(C_6F_4)_3$ did not dissolve in concentrated nitric acid until the boiling point had almost been reached when it dissolved quite readily. The solution was diluted with about twice its volume of distilled water, filtered and set aside for two days at room temperature (or overnight in a refrigerator). The mass of tiny needle-like crystals was removed from the mother liquor and washed quickly with a small amount of cold water before being dried at room temperature on a vacuum line (Found: C, 25.3, 25.3; H, 0.6, 0.6; N, 2.25, 2.15; F, 26.0. $Sb_2C_{18}F_{12}(NO_3)_2(OH)_2$ calcd.: C, 25.6; H, 0.2; N, 3.3; F, 26.6%).

The compound is soluble in warm water and when such solutions are left at room temperature for an hour or so, small bubbles of gas can be seen in the liquid. As the samples were repeatedly recrystallized the nitrogen content decreased from 2.25 to 0.8 to 0.6% and finally to about 0.3% (this final value is only approximate and represents, essentially, a nitrogen-positive test only since the determination was at the limit of sensitivity of the method). At this point the analyses corresponded to the tetrahydroxo derivative $Sb_2(C_6F_4)_3(OH)_4$ (Found: C, 28.4; H, 0.3; (N, 0.3); F, 29.9; Sb + O by difference, 41.1%; $Sb_2C_{18}F_{12}H_4O_4$ calcd.: C, 28.6; H, 0.5; N, 0.0; F, 30.2; Sb + O, 40.7%). The melting-decomposition point was not sharp and occurred at about 310 °C.

Infrared spectrum of $Sb_2(C_6F_4)_3(OH)_4$ (cm^{-1}): 1595mb, 1477sb, 1429sb, 1329w, 1310w, 1295sh, 1290w, 1262w, 1245w, 1235w, 1130w, 1107s, 1046w, 1023s, 833w, 812m, 799m, 768w, 646m, 624sb, 594m, 578msh, 546mb, 514w, 471w, 373m, 366msh, 303w, 276w.

Preparation of $Sb_2(C_6Cl_4)_3$

Antimony (1 g) and 1,2-diiodotetrachlorobenzene [9] (1 g) were heated in a sealed tube to 250 °C for 4 h. By arranging a slight temperature gradient in the oven it was possible to make most of the SbI_3 co-product distil to the colder end of the tube leaving the essentially involatile mixture of $Sb_2(C_6Cl_4)_3$ and Sb at the other. After opening the tube the product was extracted with 5 or 6 aliquots (ca. 25 cm^3) of boiling dimethylformamide; the first aliquot contains virtually all of the remaining antimony triiodide and, if very deeply coloured, may be discarded. On concentrating the extracts by boiling, the $Sb_2(C_6Cl_4)_3$ separates as tiny crystals of the hemi-solvate; the analytical sample was washed twice with acetone and dried on a vacuum line at room temperature for 1 h. (Found: C, 25.7, 25.65; H, 0.4, 0.4; N, 0.7, 0.7; Cl, 44.3. $C_{18}Cl_{12}Sb_2 \cdot 0.5DMF$ calcd.: C, 25.4; H, 0.4; N, 0.7; Cl, 46.2%). The identity of the occluded dimethylformamide was confirmed by driving off the solvent in a mass spectrometer and measuring the mass of the peak at $m/e = 73$ (observed mass, 73.0538; calculated for $^{12}C_3H_7{}^{14}N^{16}O$: 73.0528)

Infrared spectrum of $Sb_2(C_6Cl_4)_3 \cdot 0.5DMF$ (cm^{-1}): 1685sb, 1377w, 1360w, 1318shm, 1313s, 1298m, 1282s, 1264sh, 1180wb, 1146s, 1127m, 1084w, 1063s, 1037w, 842s, 817s, 656w, 640m, 586sh, 581w, 341s. Peaks which are common with a DMF mull at about the same concentration are 1685, 1084 and 656 cm^{-1}.

The solvate does not melt below 320 °C but loses the dimethylformamide above about 100 °C; on rapid heating in a tiny bunsen flame a sample held in a melting point tube first melts and then explodes with an audiable "crack". $Sb_2(C_6Cl_4)_3$ is insoluble in boiling hexane, chloroform, alcohol, ethyl acetate and acetone. It dissolves in, and may be recrystallized from, hot pyridine and hot nitrobenzene.

The product $Sb_2(C_6Cl_4)_3$ may also be extracted from the reaction residues by using 3 × 50 cm^3 aliquots of boiling nitrobenzene (after SbI_3 has been removed by boiling with 25 cm^3 of dimethylformamide). The tiny, glistening crystals obtained on boiling down the extracts contain half a mole of nitrobenzene (Found: C, 26.9; H, 0.3; N, 0.75; Cl, 45.1. $C_{18}Cl_{12}Sb_2 \cdot 0.5(C_6H_5NO_2)$ calcd.: C, 26.6; H, 0.3; N, 0.7; Cl, 45.0%).

On heating 52.8 mg of solvate in a vacuum at 150 °C for 45 min a weight loss of 3.6 mg (6.8%) was recorded; calculated for loss of half a mole of nitrobenzene, 6.5%. The remaining solid was subjected to a full microanalysis (Found: C, 24.1; H, 0.0; N, 0.0; Cl, 46.8, 47.1. $C_{18}Cl_{12}Sb_2$ calcd.: C, 24.4; H, 0.0; N, 0.0; Cl, 48.1%).

Infrared spectrum (cm^{-1}) of $Sb_2(C_6Cl_4)_3 \cdot 0.5C_6H_5NO_2$: 1526m, 1344m, 1317sh, 1311s, 1296m, 1282s, 1264sh, 1175bw, 1143s, 1126m, 1062s, 847shw, 840s, 816s, 788w, 700m, 679w, 638m, 586shw, 581w, 339s.

Infrared spectrum (cm^{-1}) of unsolvated $Sb_2(C_6Cl_4)_3$: 1311s, 1296m, 1280s, 1265sh, 1175bw, 1143s, 1126m, 839s, 814s, 639m, 580w, 339m. Thus the difference in these two spectra is slight, the solvate spectrum having additional peaks 700, 788, 1344 and 1526 cm^{-1} which correspond closely with the main absorption peaks in free nitrobenzene.

Similarly when recrystallized from pyridine or diethylformamide, $Sb_2(C_6Cl_4)_3$ separates out as hemi-solvates (Found: C, 25.65; H, 0.4; N, 0.9; Cl, 45.2. $C_{18}Cl_{12}Sb_2 \cdot 0.5C_5H_5N$ calcd.: C, 26.6; H, 0.3; N, 0.8; Cl, 46.0%. Found: C, 26.55; H, 0.7; N, 0.8; Cl, 43.4. $C_{18}Cl_{12}Sb \cdot 0.5DEF$ calcd.: C, 26.3; H, 0.6; N, 0.75; Cl, 45.5%). As can be seen from the analytical figures some problems were encountered with the accurate determination of chlorine in these polychloro-aromatic derivatives; almost always the figures obtained were 1–2% low.

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