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PAPER

Unusual neutral ligand coordination to arsenic and antimony trifluoride†

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The preparations and spectroscopic characterisation of the hydrolytically unstable As(III) complexes, $[AsF_3(OPR_3)_2]$ (R = Me or Ph) and $[AsF_3\{Me_2P(O)CH_2P(O)Me_2\}]$ are described and represent the first examples of complexes of AsF_3 with neutral ligands. The crystal structure of $[AsF_3\{Me_2P(O)CH_2P(O)Me_2\}]$ contains dimers with bridging diphosphine dioxide, but there are also long contacts between the dimers to neighbouring phosphine oxide groups, completing a very distorted six-coordination at arsenic and producing a weakly associated polymer structure. The reaction of AsF_3 with $OAsPh_3$ affords Ph_3AsF_2, and no arsine oxide complex was formed. Reaction of SbF_3 with OER_3 (R = Me or Ph, E = P or As), $Me_2P(O)CH_2P(O)Me_2$ and $Ph_2P(O)(CH_2)_nP(O)Ph_2$ (n = 1 or 2) in MeOH produces $[SbF_3(OER_3)_2]$, $[SbF_3\{Me_2P(O)CH_2P(O)Me_2\}]$ and $[SbF_3\{Ph_2P(O)(CH_2)_nP(O)Ph_2\}]$ respectively. The X-ray structures reveal that the complexes contain square pyramidal SbF_3O_2 cores with apical F and *cis* disposed pnictogen oxides. However, whilst $[SbF_3(OER_3)_2]$ (R = Ph: E = P or As; R = Me: E = As) and $[SbF_3\{Ph_2P(O)CH_2P(O)Ph_2\}]$ are monomeric, $[SbF_3\{Me_2P(O)CH_2P(O)Me_2\}]$ is a dimer with bridging diphosphine dioxides producing a twelve-membered ring, and $[SbF_3\{Ph_2P(O)(CH_2)_2P(O)Ph_2\}]$ is a chain polymer with diphosphine dioxide bridges. In the $OAsR_3$ reactions with SbF_3, R_3AsF_2 are also formed. Notably the Sb–O(P) bonds are shorter than As–O(P), despite the covalent radii (As < Sb), consistent with very weak coordination of the AsF_3. IR and multinuclear (^1H, ^{19}F and ^{31}P) NMR data are reported and discussed. BiF_3 does not react with pnictogen oxide ligands under similar conditions and halide exchange of bismuth chloro complexes with Me_3SnF gave BiF_3.

Introduction

The widely acknowledged renaissance in p-block chemistry over the last decade has included significant developments in the coordination chemistry of the heavier p-block halides (chlorides, bromides, iodides). In contrast, similar studies of the fluorides are very limited. Within Group 15, the elements, arsenic, antimony and bismuth all form trivalent and pentavalent fluorides which show varying degrees of Lewis acidity. However, they are mostly also strong fluorinating agents and hence their reactions with organic ligands can result in fluorination over coordination.[1–3]

Arsenic trifluoride is a colourless, corrosive liquid at ambient temperatures and is composed of pyramidal AsF_3 molecules in the solid state. In contrast, SbF_3 is a polymeric solid and contains a distorted six-coordinate antimony environment with three short and three long Sb–F bonds, whilst BiF_3 contains bismuth in a very distorted nine-coordinate environment.[1,2] Antimony trifluoride is widely used (usually with some added $SbCl_5$) as a fluorinating agent (Swarts reagent) for organic and inorganic chloro-compounds;[4] arsenic trifluoride also found limited use as a fluorinating agent but has been superceded by less corrosive and toxic reagents. In contrast, BiF_3 is insoluble in common solvents and inert. The only structurally characterised adducts of AsF_3 functioning as a Lewis acid appear to be $[AsF_4]^-$, $[As_2F_7]^-$ and $[As_4F_{13}]^-$,[5] whilst it behaves as a Lewis base *via* the As lone pair in $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(AsF_3)]$ and $[Au(AsF_3)SbF_6]$,[6] and as a fluorine donor ligand towards some "naked-" d, f or s block metal cations.[7] SbF_3 forms a range of fluoroanions including $[SbF_4]^-$, $[Sb_2F_7]^-$, $[Sb_3F_{10}]^-$, $[Sb_4F_{13}]^-$, $[Sb_2F_{10}]^{4-}$, $[Sb_4F_{16}]^{4-}$,[3,8–10] but only a few complexes with neutral ligands have been fully characterised, including $[SbF_3(crown)]$ (crown = 15-crown-5, 18-crown-6) and $[(SbF_3)_2(12\text{-crown-}4)]$, all of which contain pyramidal SbF_3 units weakly interacting (~3.0–3.2 Å) with the crown oxygen atoms,[11] $[SbF_3(L)]$ (L = 12,13-benzo-1,10-di(azamethyl)-4,7-dioxacyclotetradecane-11,14-dione),[12] $[SbF_3(4\text{-}MeO\text{-}C_5H_4NO)_2]$[13] and two amino acid adducts in which the amino acid bridges the five-coordinate Sb(III) atoms.[14] Bismuth(III) fluoride also forms fluoroanions with a variety of stoichiometries; these have high bismuth coordination numbers (8 or 9) and some behave as fast fluoride ion conductors,[3,15] but again there seem to be no well established examples of neutral ligand complexes.

The heavier trihalides of arsenic, antimony and bismuth, MX_3 (M = As, Sb or Bi; X = Cl, Br or I) are modest Lewis acids

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and form complexes with a variety of neutral donor ligands from Group 15 and 16.[3] The structures, although complicated in detail, are often characterised by the presence of pyramidal MX_3 or dimeric $X_2M(\mu\text{-}X)_2MX_2$ units with the remaining coordination sites occupied by weakly bound neutral ligands or bridging halides. The As, Sb or Bi based lone pairs show varying degrees of stereochemical activity (often most evident in the case of antimony); in some cases a vacant vertex site is found (assumed to be occupied by the lone pair), but in other cases the lone pair appears inactive and is presumably in the *n*s orbital. In solution in non-coordinating solvents, the complexes are typically extensively dissociated.

Here we report the results of our studies of the reactions of the AsF_3 and SbF_3 with a series of (neutral) pnictogen oxides, which were selected since the hard O-donor groups would be expected to offer the maximum likelihood of coordination to the Group 15 trifluorides. IR and multinuclear (^1H, ^{19}F and ^{31}P) NMR data are reported for all the new complexes and the crystal structures of representative examples are reported.

Results and discussion

AsF_3 Complexes

Very moisture sensitive, white powders were obtained from the reaction of AsF_3 with $OPPh_3$, $OPMe_3$ and $Me_2P(O)CH_2P(O)Me_2$ in anhydrous CH_2Cl_2 solution. These were identified by microanalysis as $[AsF_3(OPR_3)_2]$ and $[AsF_3\{Me_2P(O)CH_2P(O)Me_2\}]$. However, attempts to isolate complexes with $Ph_2P(O)(CH_2)_nP(O)Ph_2$ (n = 1, 2) were unsuccessful (the unreacted ligands being recovered), although *in situ* ^{19}F and ^{31}P NMR spectroscopic studies suggested some interaction of AsF_3 and $Ph_2P(O)CH_2P(O)Ph_2$ in CH_2Cl_2 solution. The complexes are extremely moisture sensitive especially in solution, losing AsF_3 easily. In contrast, $[AsF_3(OAsPh_3)_2]$ did not form from the reaction of AsF_3 with $OAsPh_3$, which instead produced Ph_3AsF_2 identified by its IR spectrum, the $^{19}F\{^1H\}$ chemical shift of $\delta = -89.5$, and by the unit cell of the colourless crystals isolated from the reaction mixture.[16–18] Fluorination of arsine oxides by some p-block fluorides (*e.g.* SiF_4) has been observed previously.[19]

The spectroscopic data on the AsF_3 complexes are generally similar to those of the antimony analogues (below), showing IR spectra with low frequency shifts in the $\upsilon(P{=}O)$ vibrations and strong bands in the region ~580–650 cm^{-1} assigned as terminal As–F modes.[20] The NMR spectra are consistent with exchanging systems and show a single line in the $^{31}P\{^1H\}$ NMR spectra with small positive coordination shifts. In CH_2Cl_2 solution, AsF_3 exhibits a singlet in the $^{19}F\{^1H\}$ NMR spectra at $\delta = -43.5$, and freshly prepared solutions of the complexes each show singlet resonances in the range δ ~–46 to –53, which show only small temperature drifts on cooling to 190 K. On standing in solution in CH_2Cl_2 some decomposition occurs, evidenced by the appearance of new resonances at lower frequency in the ^{19}F NMR spectra.

Needle crystals of $[AsF_3\{Me_2P(O)CH_2P(O)Me_2\}]$ were obtained directly from the reaction mixture upon cooling, and the structure (Fig. 1) reveals pyramidal AsF_3 units coordinated to bridging diphosphine dioxides to give a 12-membered ring, but in addition, there are weak O···As (2.966(2) Å) contacts from the diphosphine dioxides of neighbouring rings which complete a distorted octahedron about the arsenic atoms and lead to a weakly assembled polymer structure. The sum of the van der Waals radii of As and O is 3.4 Å. This very distorted six-coordination contrasts with the five-coordination found in the directly analogous $[SbF_3\{Me_2P(O)CH_2P(O)Me_2\}]$ (below). The As–F(1) bond, which is *trans* to the long As···O, is shorter (1.741(2) Å) than the other two (1.756(2), 1.769(2) Å), and the two shorter As–O bonds disposed *cis* are 2.575(2) and 2.633(2) Å. Notably, these bonds are longer than the Sb–O bonds in $[SbF_3\{Me_2P(O)CH_2P(O)Me_2\}]$ despite the smaller covalent radius of As (1.21 Å) compared to Sb (1.41 Å), indicating very weak As–O interactions. The P–O bonds are not significantly different in the two complexes, and only slightly lengthened from those in $Me_2P(O)CH_2P(O)Me_2$ itself (1.489(3), 1.492(3) Å).[19] The As–F bonds in solid AsF_3 are 1.699(12) to 1.721(10) Å and in the gas phase are 1.708 Å, with ∠F–As–F 92.9 to 95.5° (solid) or 95.97° (gas).[21] The structural data therefore suggest little perturbation of the AsF_3 moiety, and very weak interaction with the phosphine oxide groups, which mirrors the low stability of these complexes.

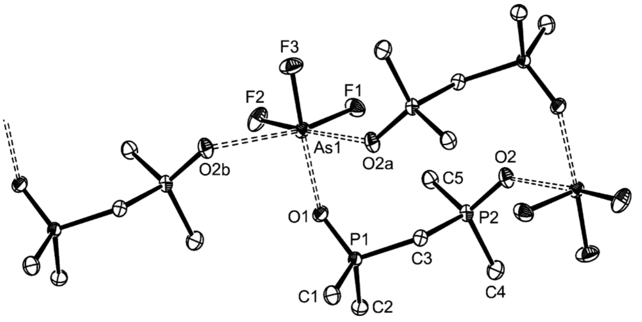

Fig. 1 View of the structure of the $[AsF_3\{Me_2P(O)CH_2P(O)Me_2\}]$ polymer with atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): As1–F1 = 1.7414(15), As1–F2 = 1.7562(15), As1–F3 = 1.7587(15), As1–O1 = 2.5750(17), As1–O2a = 2.6327(17), As1–O2b = 2.9655(18), P1–O1 = 1.4978(17), P2–O2 = 1.5029(17), F1–As1–F2 = 92.64(7), F1–As1–F3 = 90.48(7), F2–As1–F3 = 90.98(8), F1–As1–O1 = 80.68(6), F2–As1–O1 = 80.86(6), F1–As1–O2a = 84.55(7), F3–As1–O2a = 87.54(7), O1–As1–O2a = 100.13(6), F2–As1–O2b = 83.93(6), F3–As1–O2b = 79.72(6), O1–As1–O2b = 108.41(5), O2a–As1–O2b = 98.57(5). Symmetry operations: a = 1 $-x$, 1 $-y$, $-z$; b = x, 1 + y, z.

SbF_3 Complexes

White solids formulated as $[SbF_3(OPR_3)_2]$ (R = Me or Ph) and $[SbF_3\{R_2P(O)(CH_2)_nP(O)R_2\}]$ (R = Ph or Me: n = 1; R = Ph: n = 2) were obtained by stirring solutions of anhydrous SbF_3 and the appropriate ligand in anhydrous methanol for several hours. The reactions did not occur on stirring the ligand with a suspension of SbF_3 in CH_2Cl_2, and were incomplete in MeCN solution. Similarly, $[SbF_3(OAsR_3)_2]$ (R = Me or Ph) were obtained from methanol solution, although the reactions are less clean. In addition to the formation of $[SbF_3(OAsR_3)_2]$, variable amounts of R_3AsF_2 are also formed, readily identified by their characteristic IR spectra[16] and ^{19}F NMR chemical shifts[17,22] (R = Ph: $\delta = -89.6$; R = Me: $\delta = -53.6$). The R_3AsF_2 can be removed by careful washing with *n*-hexane, or recrystallisation. Attempts to isolate complexes with softer neutral sulfur ligands, including Ph_3PS and $MeS(CH_2)_2SMe$,

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under similar reaction conditions were unsuccessful. This is in marked contrast to the ready formation of several series of complexes of the heavier SbX_3 (X = Cl, Br or I) with neutral S- and Se-donor ligands.[23–28]

In contrast to the AsF_3 systems above, the SbF_3 phosphine- and arsine-oxide complexes are mostly white powders or colourless crystals, not appreciably moisture-sensitive in the solid state, and modestly soluble in anhydrous CH_2Cl_2, MeCN or MeOH. Spectroscopic data provided limited structural information, and thus we also undertook X-ray crystal structure analyses for several of the new complexes, since no literature data exist in this area. In fact, we find that although the structures with the different ligands differ in detail, all are based upon a square pyramidal SbF_3O_2 core with apical F, the "free site" presumably accommodating a stereochemically active lone pair. A similar SbF_5 core geometry is found in many fluoroantimonate(III) structures.[9]

The structure of $[SbF_3(OAsMe_3)_2]$ (Fig. 2) shows a discrete square pyramidal molecule with an apical fluorine (Sb–F(1) = 1.943(2) Å) and the antimony lying below the base plane, which results in all the angles involving F(1) being < 90°. The basal Sb–F bonds are slightly longer (Sb–F = 2.002(2), 2.010(2) Å) with the angle between the *cis* fluorines (F(2) and F(3)) of 84.69(10)°. The Sb–F bond lengths may be compared with the three shortest bonds in solid SbF_3 (1.94(2)–1.90(2) Å).[29] The O–Sb–O angle is 99.9(1)° and *d*(As–O) = 1.680(3), 1.692(3) Å. Crystal structures were also obtained for $[SbF_3(OAsPh_3)_2]$ and $[SbF_3(OPPh_3)_2]$ and both are similar square pyramidal monomers with apical fluorine and *cis* disposed pnictogen oxides (Fig. 3). Both sets of crystals were twinned, and while for $[SbF_3(OAsPh_3)_2]$ the pseudo-merohedral twinning was modelled satisfactorily, this was less successful for $[SbF_3(OPPh_3)_2]$‡ (see Experimental Section), hence only the former is described in detail.

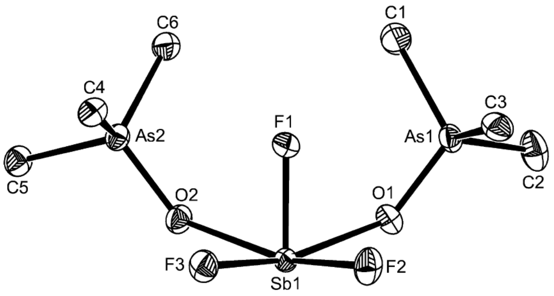

Fig. 2 View of the structure of $[SbF_3(OAsMe_3)_2]$ with atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sb1–F1 = 1.943(2), Sb1–F2 = 2.002(2), Sb1–F3 = 2.010(2), Sb1–O1 = 2.238(3), Sb1–O2 = 2.276(3), As1–O1 = 1.680(3), As2–O2 = 1.692(3), F1–Sb1–F2 = 83.69(10), F1–Sb1–F3 = 83.83(10), F2–Sb1–F3 = 84.63(10), F1–Sb1–O1 = 80.07(10), F2–Sb1–O1 = 85.46(10), F1–Sb1–O2 = 80.50(10), F2–Sb1–O2 = 162.12(11), F3–Sb1–O1 = 161.91(10), F3–Sb1–O2 = 85.42(10), O1–Sb1–O2 = 99.89(10).

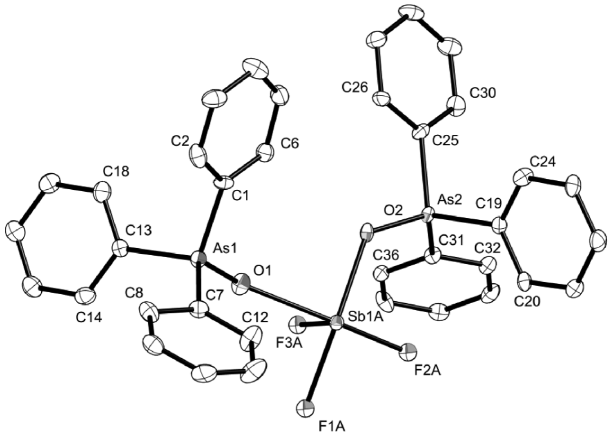

Fig. 3 View of the structure of $[SbF_3(OAsPh_3)_2]$ showing the major component of the disorder, with atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sb1a–F1a = 2.10(2), Sb1a–F2a = 1.96(3), Sb1a–F3a = 1.918(13), Sb1a–O1 = 2.363(6), Sb1a–O2 = 2.300(5), As1–O1 = 1.666(5), As2–O2 = 1.682(5), F1a–Sb1a–F2a = 83.5(10), F1a–Sb1a–F3a = 71.8(6), F2a–Sb1a–F3a = 88.2(7), F1a–Sb1a–O1 = 93.4(6), F1a–Sb1a–O2 = 151.2(5), F2a–Sb1a–O1 = 162.0(6), F2a–Sb1a–O2 = 84.7(8), F3a–Sb1a–O1 = 74.0(4), F3a–Sb1a–O2 = 81.7(8), O2–Sb1a–O1 = 89.8(2).

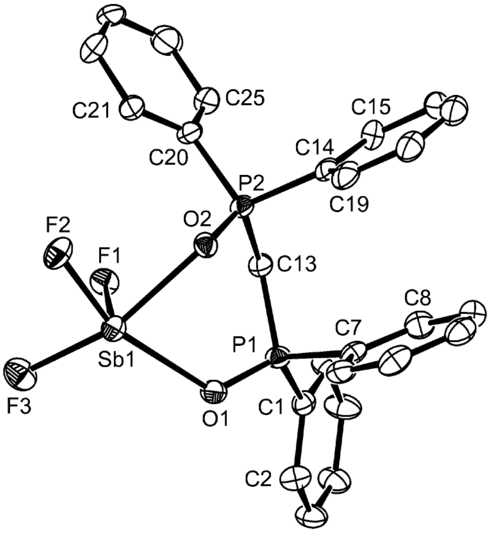

Fig. 4 View of the structure of $[SbF_3\{Ph_2P(O)CH_2P(O)Ph_2\}]$ with atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sb1–F1 = 1.916(3), Sb1–F2 = 1.921(3), Sb1–F3 = 2.018(3), Sb1–O1 = 2.593(3), Sb1–O2 = 2.306(3), P1–O1 = 1.493(4), P2–O2 = 1.508(4), F1–Sb1–F2 = 90.17(13), F1–Sb1–F3 = 81.68(13), F2–Sb1–F3 = 88.40(13), F1–Sb1–O1 = 78.27(12), F1–Sb1–O2 = 78.01(12), F2–Sb1–O1 = 160.21(12), F2–Sb1–O2 = 83.85(13), F3–Sb1–O1 = 105.49(12), F3–Sb1–O2 = 158.20(12), O1–Sb1–O2 = 78.10(11).

The structure of $[SbF_3\{Ph_2P(O)CH_2P(O)Ph_2\}]$ (Fig. 4) shows a very distorted square pyramidal monomer with apical fluoride and a chelating diphosphine dioxide, which is asymmetrically coordinated (Sb–O = 2.306(3), 2.593(3) Å). The antimony lies slightly below the basal plane which is distorted by the wide F3–Sb–O1 angle of 105.49(12)°. The chloro analogue $[SbCl_3\{Ph_2P(O)CH_2P(O)Ph_2\}]$ is known and is also square pyramidal,[24] but much less distorted. The reasons for the distortion are unclear; there are no short contacts to neighbouring molecules and similar distortions are not found in the other structures reported below.

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‡ Crystal of $[SbF_3(OPPh_3)_2]$: monoclinic, *Cc*, $a = 10.1140(7)$, $b = 32.559(2)$, $c = 10.8680(7)$ Å, $\beta = 117.732(3)$°.

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The structure of [$SbF_3\{Me_2P(O)CH_2P(O)Me_2\}$] also contains a square pyramidal antimony geometry, but in this case the diphosphine dioxides are bridging to give a discrete dimer containing a twelve-membered ring (Fig. 5). The geometry at antimony replicates the key features found in [$SbF_3(OAsR_3)_2$] (above). The P–O distances (1.507(3) to 1.509(3) Å) are only slightly longer than in the ligand itself (1.489(3), 1.492(3) Å).[19] The nearest contact to the open face of the pyramid is an oxygen from a neighbouring molecule at >4.3 Å, which is significantly greater than the sum of the van der Waals radii (3.6 Å); thus the square pyramidal description seems fully justified.

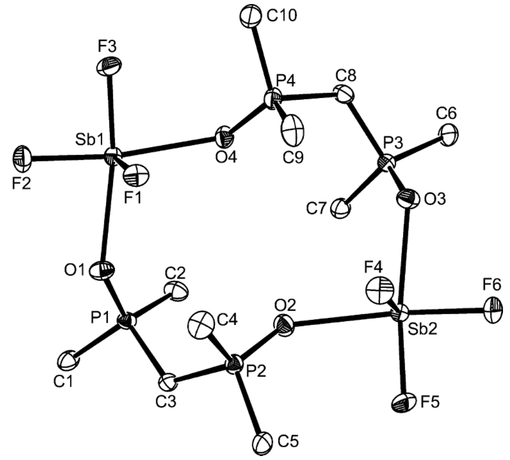

Fig. 5 View of the dimer present in the crystal structure of [$SbF_3\{Me_2P(O)CH_2P(O)Me_2\}$] with atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sb1–F1 = 1.914(2), Sb1–F2 = 1.970(2), Sb1–F3 = 1.972(2), Sb2–F4 = 1.909(2), Sb2–F5 = 1.964(2), Sb2–F6 = 1.971(2), Sb2–O1 = 2.446(3), Sb1–O4 = 2.416(3), Sb2–O3 = 2.411(3), Sb2–O2 = 2.455(3), P1–O1 = 1.508(3), P2–O2 = 1.509(3), P3–O3 = 1.508(3), P4–O4 = 1.507(3), F1–Sb1–F2 = 87.46(10), F1–Sb1–F3 = 85.83(9), F2–Sb1–F3 = 84.53(9), F1–Sb1–O4 = 82.24(9), F3–Sb1–O4 = 84.07(9), F1–Sb1–O1 = 77.90(9), F2–Sb1–O1 = 82.26(9), O1–Sb1–O4 = 105.83(9), F4–Sb2–F5 = 85.71(10), F4–Sb2–F6 = 88.72(10), F5–Sb2–F6 = 85.04(10), F4–Sb2–O3 = 78.81(10), F6–Sb2–O3 = 84.47(10), F4–Sb2–O2 = 81.61(9), F5–Sb2–O2 = 87.05(9), O2–Sb2–O3 = 100.59(9).

A third structural type is provided by [$SbF_3\{Ph_2P(O)(CH_2)_2P(O)Ph_2\}$] which also contains square pyramidal SbF_3O_2 units, but in this case the diphosphine dioxide bridges adjacent Sb atoms producing an infinite chain structure (Fig. 6). The bond lengths and angles parallel those in the other structures. In all of the pnictogen oxide complexes, the Sb–O distances are much shorter than those found in [SbF_3(crown)], which are typically ≥ 3 Å,[11] but similar to those in [$SbF_3(4\text{-}MeO\text{-}C_5H_4NO)_2$].[13]

The IR spectra of the phosphine- and arsine-oxide complexes show the υ(PO) and υ(AsO) frequencies are too low a frequency compared to the ligands themselves, and exhibit two or three strong absorptions in the region ~560–470 cm^{-1} (Experimental Section) which we assign to terminal Sb–F bonds.[30] The solution $^{31}P\{^1H\}$ NMR spectra each show singlet resonances, with small high frequency coordination shifts and the spectra are essentially unchanged on cooling the solutions to 190 K. Similarly, the $^{19}F\{^1H\}$ NMR spectra show singlets in the range ~ −70 to −80 ppm, again little affected by cooling the solutions. These values are similar to those observed for various fluoroantimonates(III) in aqueous solution,[10] which suggests that the Sb–F are the dominant interactions. The solution spectra do not reflect the inequivalent fluorine positions evident in the solid structures. This indicates either fluxionality in solution, or, more likely, rapid dissociation/exchange which continues even at low temperatures.

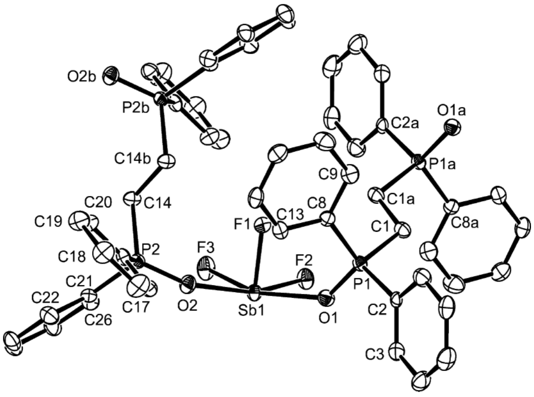

Fig. 6 View of the part of the polymer structure of [$SbF_3\{Ph_2P(O)(CH_2)_2P(O)Ph_2\}$] with atom numbering scheme and showing the coordination environment at antimony. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sb1–F1 = 1.906(3), Sb1–F2 = 1.979(3), Sb1–F3 = 1.952(3), Sb1–O1 = 2.456(3), Sb1–O2 = 2.385(4), P1–O1 = 1.507(4), P2–O2 = 1.504(4), F1–Sb1–F3 = 87.00(13), F1–Sb1–F2 = 86.50(13), F2–Sb1–F3 = 86.84(13), F1–Sb1–O1 = 77.97(12), F1–Sb1–O2 = 79.19(13), F2–Sb1–O1 = 83.22(12), F2–Sb1–O2 = 163.43(13), F3–Sb1–O1 = 162.42(13), F3–Sb1–O2 = 84.12(13), O1–Sb1–O2 = 101.71(12).

BiF_3 Complexes

No reaction occurred on refluxing suspensions of BiF_3 in MeOH or MeCN with the pnictogen oxide ligands. On overnight stirring of a solution of [$BiCl_3(OPPh_3)_3$][31] in CH_2Cl_2 with three equivalents of Me_3SnF, the latter slowly dissolved and then a fine white precipitate formed. The precipitate was identified as BiF_3 by its IR spectrum. On removing the solvent from the filtrate, a white solid was obtained which was identified by IR, ^1H and $^{31}P\{^1H\}$ NMR spectroscopy as [$Me_3SnCl(OPPh_3)$].[32] Reaction of [$BiCl_3\{Ph_2P(O)CH_2P(O)Ph_2\}$][31] and Me_3SnF also produced BiF_3. It is clear therefore that pnictogen oxides do not react directly with the polymeric BiF_3. Also, the neutral ligands do not bind sufficiently strongly to the Bi(III) centre in molecular complexes to prevent BiF_3 precipitating from chloride/fluoride exchange reactions. Similar behaviour has been seen in some d-block fluoride systems.[33]

Conclusions

The first examples of Lewis acid complexes of AsF_3 with neutral ligands have been prepared and fully characterised, together with a series of SbF_3 analogues. The results demonstrate that both AsF_3 and SbF_3 are modest Lewis acids towards neutral oxygen donor ligands, but in contrast to the analogues containing heavier halogens they did not form isolable complexes with softer, neutral sulfur ligands. Their tendency to behave as fluorinating agents is illustrated by the formation of F_2AsR_3 in their reaction

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with $OAsR_3$. Although its coordination chemistry has been little studied prior to this work, we note that AsF_3 is highly unusual in coordinating in three different ways: as a Lewis base *via* the lone pair on As,[6] as an F-donor ligand *via* the As-coordinated fluorides,[7] and as a Lewis acid towards appropriate neutral ligands as established here. It seems likely that with careful choice of ligand structure, a wider range of complexes may exist, despite the competition from fluorination reactions. The absence of Lewis base adducts of BiF_3, reflects the inability of the pnictogen oxides to compete with formation of insoluble polymeric BiF_3.

Experimental section

General: All reactions were conducted using Schlenk, vacuum line and glove-box techniques and under a dry dinitrogen atmosphere. Solvents were dried by distillation from magnesium turnings (MeOH) or CaH_2 (MeCN, CH_2Cl_2). SbF_3 and BiF_3 were obtained from Aldrich and used as received. AsF_3 was made from As_2O_3 and HSO_3F and purified by distillation under dinitrogen.[34] $OPMe_3$ (Strem) was freshly sublimed *in vacuo*. $OPPh_3$ and $OAsPh_3$ (Aldrich) were heated *in vacuo*. $OAsMe_3$ and $R_2P(O)(CH_2)_nP(O)R_2$ ($n = 1$ or 2) were made as described.[19,35,36] IR spectra were recorded as Nujol mulls using CsI plates on a Perkin Elmer Spectrum 100 spectrometer, ^{1}H NMR spectra in $CDCl_3$ or CD_2Cl_2 solutions on a Bruker AV300, $^{31}P\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR spectra on a Bruker DPX400 and referenced to external 85% H_3PO_4 and $CFCl_3$, respectively. Microanalytical measurements were performed by Medac Ltd.

$[AsF_3(OPPh_3)_2]$: A solution of $OPPh_3$ (0.55 g, 1.97 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a CH_2Cl_2 (5 mL) solution of AsF_3 (0.13 g, 0.98 mmol). The colourless reaction mixture was stirred for 3 h. A white solid was obtained on concentrating the solution; this was filtered off, washed with hexane (5 mL) and dried *in vacuo.* Yield: 0.45 g, 63%. Required for $C_{36}H_{30}AsF_3O_2P_2\cdot\frac{1}{2}CH_2Cl_2$ (731.0): C 60.0, H 4.3; found: C 59.3, H 4.6%. ^{1}H NMR ($CDCl_3$, 293 K): $\delta = 5.3$ (s) CH_2Cl_2, 7.4–7.7 (m). $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 293 K): $\delta = -51.7$ (s), (190 K) −53.0 (s). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 293 K): $\delta = 32.0$ (s); (195 K): 31.3 (s). IR (Nujol): $\upsilon = 1153$ (br), ($P{=}O$), 610 (m), 585 (m) (AsF) cm^{-1}

$[AsF_3(OPMe_3)_2]$: Was made similarly to the $OPPh_3$ complex, as a waxy white solid. Yield: 50%. Required for $C_6H_{18}AsF_3O_2P_2\cdot\frac{1}{2}CH_2Cl_2$ (358.5): C 21.8, H 5.3; found: C 21.6, H 4.6%. ^{1}H NMR ($CDCl_3$, 293 K): $\delta = 1.51$ (d, $^{2}J_{PH} = 15$ Hz), 5.3 (s) CH_2Cl_2. $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2, 293 K): $\delta = -52.5$, (200 K) −53.0. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 293 K): $\delta = 43.8$ (s); (190 K): 44.7 (s). IR (Nujol): $\upsilon = 1148$ (vbr), 1120 (sh) ($P{=}O$), 610 (sh), 596 (s) (AsF) cm^{-1}.

$[AsF_3\{Me_2P(O)CH_2P(O)Me_2\}]$: A solution of AsF_3 (0.16 g, 1.2 mmol) in CH_2Cl_2 (5 mL) was added dropwise to the CH_2Cl_2 (10 mL) solution of $Me_2P(O)CH_2P(O)Me_2$ (0.21 g, 1.2 mmol). The colourless reaction mixture was stirred for 1 h. A white solid along with some needle shaped crystals were obtained on concentrating the solution. The solid was filtered off and dried *in vacuo.* Yield: 0.30 g, 80%. Required for $C_5H_{14}AsF_3P_2O_2$ (302.0): C 20.0, H 4.7; found: C 20.7, H 5.6%. ^{1}H NMR ($CDCl_3$, 295 K): $\delta = 1.69$ (d, $^{2}J_{PH} = 15$ Hz, [12H]), 2.34 (t, $^{2}J_{PH} = 12$ Hz, [2H]). $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 293 K): $\delta = -46.0$ (s); (295 K): −48.5 (s). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 293 K): $\delta = 39.6$ (s), (190 K) 43.0 (s). IR (Nujol): 1135 (s) ($P{=}O$), 65 3(m), 598 (s), 580 (s) (AsF) cm^{-1}.

$[SbF_3(OPPh_3)_2]$: SbF_3 (0.16 g, 0.9 mmol) was dissolved in anhydrous MeOH (10 mL) and $OPPh_3$ (0.51 g, 1.8 mmol) in MeOH (5 mL) was added dropwise and the solution stirred overnight. On concentration *in vacuo* a white solid separated out, which was filtered off, rinsed with *n*-hexane (5 mL) and dried *in vacuo*. Yield: 0.62 g, 90%. Required for $C_{36}H_{30}F_3O_2P_2Sb\cdot MeOH$ (767.4): C 57.9, H 4.8; found: C 57.8, H 3.8%. ^{1}H NMR ($CDCl_3$, 293 K): $\delta = 7.5$–7.7 (m), 4.4 (s) MeOH. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 293 K): $\delta = 32.6$ (br s); (200 K): 34.1 (s). $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 293 K): $\delta = -78.2$ (s); (223 K): −79.0 (s); (183 K): −80.1 (s). IR (Nujol): $\upsilon = 1141$ (vs, br) ($P{=}O$), 542 (s), 508 (s) (SbF) cm^{-1}.

$[SbF_3(OPMe_3)_2]$: SbF_3 (0.19 g, 1.08 mmol) was dissolved in anhydrous MeOH (10 mL) and $OPMe_3$ (0.20 g, 2.17 mmol) in MeOH (10 mL) was added dropwise and the solution stirred overnight. The colourless solution was concentrated to ~ 5 mL and *n*-hexane (5 mL) added and the mixture refrigerated. The white solid which deposited was filtered off, washed with *n*-hexane (5 mL) and dried *in vacuo*. Block crystals were obtained by layering the filtrate with *n*-hexane. Yield: 0.35 g, 91%. Required for $C_6H_{18}F_3O_2P_2Sb$ (362.9): C 19.9, H 5.0; found: C 19.4, H 4.9%. ^{1}H NMR ($CDCl_3$, 293 K): $\delta = 1.55$ (d, $^{2}J_{PH} = 14$ Hz). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 293 K): $\delta = 45.5$ (s); (200 K): 48.9 (s). $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 293 K): $\delta = -78.6$ (s); (200 K): −79.9 (s). IR (Nujol): $\upsilon = 1137$ (vs, br) ($P{=}O$), 556 (s), 542 (s), 507 (s), 489 (m) (SbF) cm^{-1}.

$[SbF_3\{Me_2P(O)CH_2P(O)Me_2\}]$: SbF_3 (0.24 g, 1.34 mmol) was dissolved in anhydrous MeOH (10 mL) and $Me_2P(O)CH_2P(O)Me_2$ (0.23 g, 1.36 mmol) in MeOH (5 mL) was added dropwise and the solution stirred overnight. On concentration *in vacuo* a white solid separated out, which was filtered off, rinsed with *n*-hexane (5 mL) and dried *in vacuo*. Yield: 0.32 g, 68%. Required for $C_5H_{14}F_3O_2P_2Sb$ (346.9): C 17.3, H 4.1; found: C 17.4, H 3.6%. ^{1}H NMR ($CDCl_3$, 293 K): $\delta = 1.73$ (d, [12H], $^{2}J_{PH} = 12$ Hz), 2.32 (t, [2H] $^{2}J_{PH} = 12$ Hz). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 293 K): $\delta = 43.5$ (s); (200 K): 42.6 (s). $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 293 K): $\delta = -77.8$ (s); (200 K): −78.2 (s). IR (Nujol): $\upsilon = 1144$ (vs, br), 1093 (s) ($P{=}O$), 556 (s), 513 (s), 484 (s) (SbF) cm^{-1}.

$[SbF_3\{Ph_2P(O)CH_2P(O)Ph_2\}]$: SbF_3 (0.18 g, 1.00 mmol) was dissolved in anhydrous MeOH (10 mL) and $Ph_2P(O)CH_2P(O)Ph_2$ (0.41 g, 1.00 mmol) in MeOH (10 mL) was added and the solution stirred overnight. An off-white solid separated out, which was filtered off, washed with *n*-hexane and dried *in vacuo*. Very pale yellow block crystals were obtained from refrigerating the filtrate. Yield: 0.39 g, 66%. Required for $C_{25}H_{22}P_2O_2F_3Sb\cdot\frac{1}{4}CH_2Cl_2$ (616.3): C 49.2, H 3.7; found: C 49.2, H 3.9%. ^{1}H NMR ($CDCl_3$, 293 K): $\delta = 3.64$ (t, [2H], $^{2}J_{PH} = 12$ Hz), 5.3 (s) CH_2Cl_2, 7.2–7.9 (m, [20H]). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 293 K): $\delta = 28.8$ (s); (200 K): 29.6 (s). $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 293 K): $\delta = -74.5$ (s); (200 K): −76.5 (s). IR (Nujol): $\upsilon = 1156$ (vs, br), 1092 (m) ($P{=}O$), 532 (s), 503 (s) (SbF) cm^{-1}.

$[SbF_3\{Ph_2P(O)(CH_2)_2P(O)Ph_2\}]$: Was made similarly to the previous complex above, giving a white powder. Yield: 82%. Colourless block crystals were obtained by layering the filtrate from the preparation with *n*-hexane and refrigerating. Required for $C_{26}H_{24}F_3O_2P_2Sb\cdot CH_2Cl_2$ (694.1): C 46.7, H 3.9; found: C 47.7, H 4.1%. ^{1}H NMR ($CDCl_3$, 293 K): $\delta = 2.75$ (br,s [4H]), 5.3 (s)

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Table 1 Crystallographic parameters[a]

Compound	$[AsF_3\{Me_2P(O)CH_2P(O)Me_2\}]$	$[SbF_3(OAsMe_3)_2]$	$[SbF_3(OAsPh_3)_2]$	$[SbF_3\{Ph_2P(O)CH_2P(O)Ph_2\}]$	$[SbF_3\{Me_2P(O)CH_2P(O)Me_2\}]$	$[SbF_3\{Ph_2P(O)(CH_2)_2P(O)Ph_2\}]$
Formula	$C_5H_{14}AsF_3O_2P_2$	$C_6H_{18}As_2F_3O_2Sb$	$C_{36}H_{30}As_2F_3O_2Sb$	$C_{25}H_{22}F_3O_2P_2Sb$	$C_{10}H_{28}F_6O_4P_4Sb_2$	$C_{26}H_{24}F_3O_2P_2Sb$
M	300.02	450.79	823.19	595.12	693.70	609.14
Crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	Cc (no. 9)	$P2_12_12_1$ (no. 19)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
A (Å)	7.7004(10)	8.1563(10)	10.0551(3)	11.4165(15)	17.8949(15)	9.7891(15)
B (Å)	8.1617(15)	13.546(2)	32.8259(10)	13.335(2)	8.4721(10)	11.664(2)
C (Å)	9.7109(15)	12.4707(15)	10.7878(3)	15.599(2)	16.1193(15)	12.503(2)
α (°)	76.455(2)	90	90	90	90	65.839(10)
β (°)	78.429(2)	97.531(10)	116.5420(10)	90	109.908(5)	77.987(10)
γ (°)	65.015(2)	90	90	90	90	80.634(10)
U (Å^3)	534.22(15)	1366.0(3)	3185.43(16)	2374.7(6)	2297.8(4)	1269.3(4)
Z	2	4	4	4	4	2
μ(Mo-Kα) (mm^{-1})	3.491	6.840	2.978	1.341	2.690	1.256
Total no. reflections	11357	17429	13457	17960	25860	21763
R_{int}	0.038	0.046	0.046	0.054	0.043	0.068
Unique reflections	2446	3124	5159	5133	5254	5825
No. of parameters, restraints	122, 0	133, 0	398, 2	299, 0	235, 0	307, 0
$R_1[I_o > 2\sigma(I_o)]$	0.028	0.029	0.041	0.043	0.033	0.059
R_1 (all data)	0.036	0.037	0.045	0.052	0.041	0.084
$wR_2[I_o > 2\sigma(I_o)]$	0.054	0.064	0.104	0.078	0.062	0.104
wR_2 (all data)	0.057	0.068	0.108	0.083	0.066	0.115

[a] Common items: $T = 120$ K; λ(Mo-Kα) = 0.71073 Å; $\theta_{(max)} = 27.5°$; $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$.

CH_2Cl_2, 7.4–7.9 (m, [20H]). $^{31}P\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 293 K): $\delta = 38.6$ (s); (200 K): 39.3 (s). $^{19}F\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 293 K): $\delta = -76.8$ (s); (200 K): −77.1 (s). IR (Nujol): $\upsilon = 1146$ (vs, br), 1084 (s) (P═O), 534 (s), 501 (s) (SbF) cm^{-1}.

$[SbF_3(OAsMe_3)_2]$: SbF_3 (0.19 g, 1.08 mmol) was dissolved in anhydrous MeOH (10 mL) and $OAsMe_3$ (0.30 g, 2.2 mmol) in MeOH (10 mL) was added dropwise and the solution stirred overnight. The colourless solution was evaporated to dryness, and treated with CH_2Cl_2 (5 mL) and *n*-hexane (5 mL), which deposited a white solid on stirring. The solid was filtered off, rinsed with *n*-hexane and dried *in vacuo*. Block crystals were obtained by refrigerating the filtrate. Yield: 0.35 g. Required for $C_6H_{18}As_2F_3O_2Sb$ (450.8): C 16.0, H 4.0; found: C 16.3, H 4.2%. ^1H NMR ($CDCl_3$, 293 K): $\delta = 1.64$ (s).$^{19}F\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 293 K): $\delta = -70.7$ (s); (213 K): −70.0 (br). IR (Nujol): $\upsilon = 799$ (vs, br) (As═O), 554 (s), 515 (s) (SbF) cm^{-1}.

$[SbF_3(OAsPh_3)_2]$: SbF_3 (0.16 g, 0.9 mmol) was dissolved in anhydrous MeOH (10 mL) and $OAsPh_3$ (0.57 g, 1.8 mmol) in MeOH (5 mL) was added dropwise and the solution stirred overnight. On concentration *in vacuo* a white solid separated out, which was filtered off, rinsed with *n*-hexane (5 mL) and dried *in vacuo*. Yield: 0.40 g, 60%. Block shaped crystals were obtained from refrigerating the filtrate. Required for $C_{36}H_{30}As_2F_3O_2Sb$ (823.2): C 52.5, H 3.8; found: C 50.5, H 4.2%; several different batches of this compound gave consistently low C analyses, although spectroscopically the complex appeared pure. ^1H NMR ($CDCl_3$, 293 K): $\delta = 7.5$–7.7 (m). $^{19}F\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, 293 K): $\delta = -73.3$ (br). IR (Nujol): $\upsilon = 801$ (vs, br) (As═O), 542 (s), 508 (s), (SbF) cm^{-1}.

X-Ray Crystallography Details of the crystallographic data collection and refinement parameters are given in Table 1. Crystals suitable for single crystal X-ray analysis were obtained as described above. Data collections used a Bruker-Nonius Kappa CCD diffractometer fitted with monochromated Mo-Kα radiation (λ = 0.71073 Å), with the crystals held at 120 K in a nitrogen gas stream. Structure solution and refinement were mostly straightforward,[37–39] except for $[SbF_3(OEPh_3)_2]$ (E = As, P). E = As was solved in the non-centrosymmetric space-group *Cc* with an absolute structure parameter of 0.076(15). The coordination sphere about the metal was modelled as disordered (*ca.* 35/65) about a pseudo mirror plane located normal to the Sb–F_{ax} bond just above the metal. Split atom pairs were constrained to have the same atomic displacement parameters. An initial (poor) refinement of E = P was obtained with the coordinates from E = As, subsequent analysis of the most disagreeing F_o/F_c values[38] revealed the twin law [−1 0 0, 0 −1 0, 1 0 1]. Application of this dramatically improved the agreement indices, but a full anisotropic refinement free from constraints/restraints was not possible (indicating the possibility of further additional twinning).

CCDC 803403–803408 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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