Fluoride binding by a neutral organoantimony(V) Lewis acid embedded within a dibenzodithiophene chromophore

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Dedicated to Prof. Dr. Dr. h. c. Hubert Schmidbaur on the occasion of his 90th birthday.

Abstract: Organoantimony Lewis acids have been coveted for their ability to bind hard anions like fluoride in competing media. Herein, we report the synthesis of phenyl dithienostibole **1**, which finds an antimony(III) center embedded within a planar dithiophene chromophore. **1** also exhibits facile oxidation chemistry, reacting with tetrachloroquinone to form catecholatostiborane **2** and with *tert*-butyl peroxide in the presence of perfluoropinacol to form pinacolatostiborane **3**. **2** was then found to have a high fluoridophilicity upon UV-vis titrations affording a $K(F^-) > 10^7\ M^{-1}$. DFT calculations show that the σ*(Sb-C) orbital is the likely source of the high Lewis acidity of **2** as the fluoride anion engages with this low-lying σ*(Sb-C) orbital during binding.

Introduction

Antimony derivatives have become valuable platforms for anion sensing and transport.[1] While antimony(III) derivatives can exhibit some anion affinity and activity, especially when electron-withdrawing groups are attached to the antimony center,[2] a more practical approach involves the use of antimony(V) derivatives. Early examples involve the study of simple systems such as the tetramethylstibonium cation which was described for its ability to bind with the acetate anion.[3] While other stibonium cations have now been developed as anion complexing agents,[4] our research has recently focused on the use of neutral stiboranes. The stiboranes are typically accessed through the oxidation of stibines with *ortho*-quinones, a strategy developed several decades ago[5] and adopted more broadly in recent years[6] including by our group.[7] These endeavors have led to the discovery of antimony-based platforms that can detect anions, such as fluoride at sub-ppm concentrations[4b, 8] and transport halides[8-9] and hydroxide[8, 10] anions across phospholipid bilayers.

For sensing applications, it is important to incorporate molecular platforms that provide a measurable readout to signal anion binding at the antimony center. Previous approaches have used chromophores such as anthryl,[4b] alizarin red,[11] or BODIPY,[4e] as seen in compounds **A**-**C** (**Figure 1**). Building on this work, we have also decided to explore whether antimony-based sensing platforms could also be obtained using a dibenzodithiophene system. This effort was motivated by the fact that such derivatives are geometrically constrained due to the incorporation of the antimony center in a five-membered ring, which should elevate the Lewis acidity of the antimony center.[12] Oxidation of these species with *ortho*-quinones further restricts their geometry by incorporating the antimony in a spirocyclic arrangement, which enhances the aforementioned structural effects.

Other anticipated favorable attributes of the dibenzothiophene ligand stem from the optoelectronic properties it can impart to main group derivatives.[13] Such a possibility is exemplified in the work of Baumgartner and co-workers who generated **D**,[14] a phosphole chromophore whose photophysical properties could be modulated by the oxidation of the phosphorus

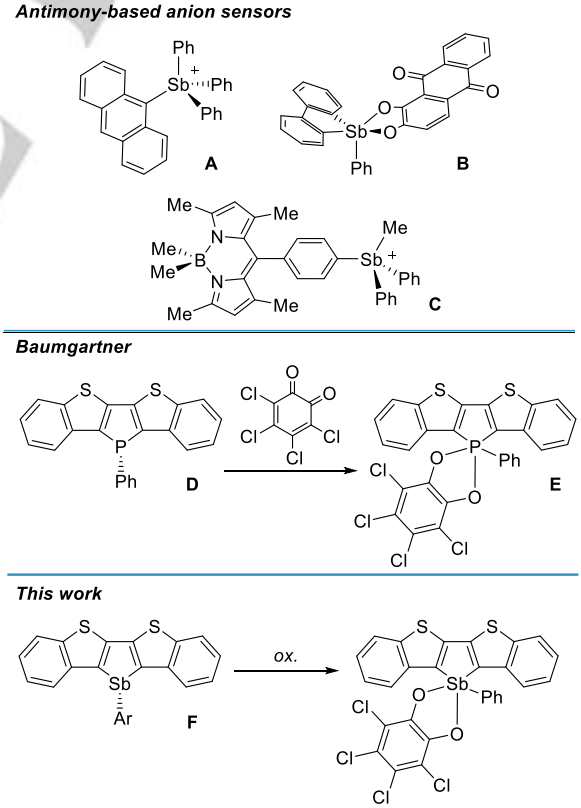

Figure 1. Top: Antimony-based anion receptors **A**-**C** previously investigated by our group. Middle: the work of Baumgartner on dithienophosphole **D** and its oxidation to catecholatophosphorane **E**. Bottom: invesitgative framework of this study involving the oxidation of stibines of type **F**.

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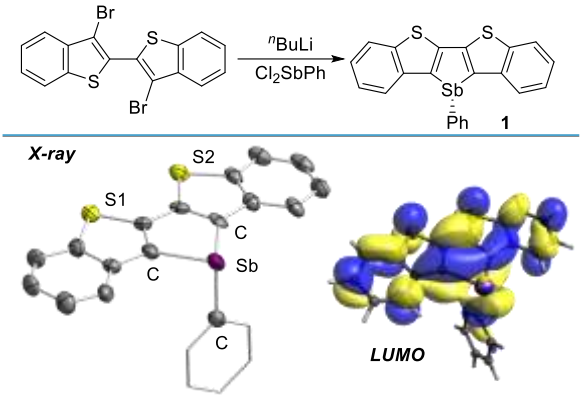
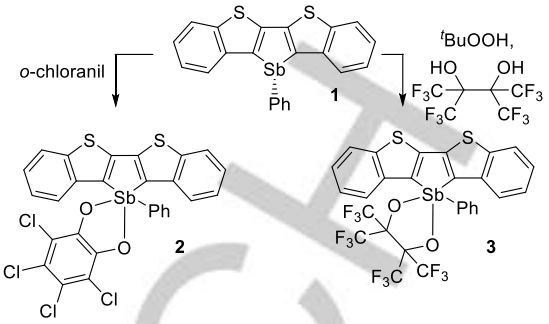


Figure 2. Top: Synthetic scheme to form dithienostibole **1**. Bottom: Solid-state structure of **1**. Hydrogen atoms and interstitial THF molecule omitted for clarity. Inset shows the LUMO of **1** (isovalue: 0.02).

center or *via* coordination to a metal center. The same group also showed that oxidizing **D** with *o*-chloranil yielded the neutral catecholatophosphorane **E** which displays latent Lewis acidity.[15] In parallel, Ohshita and co-workers synthesized and characterized analogous dithienostiboles, including those of type **F**[16] and related dithienobismoles,[17] as well as their uncyclized analogs.[18] That said, the higher valent chemistry of **F**-type compounds has not been explored. Herein, we connect these two lines of inquiry with the phenyl-substituted dithienostibole **1**, and report its oxidation chemistry and subsequent fluoride binding behavior.

Results and Discussion

The synthesis of stibole **1** is shown in **Figure 2**, in which the 2,2'-di(3-bromobenzo[*b*]thiophene) ligand was treated with 2.2 equiv. of ^{n}BuLi in the presence of TMEDA and was quenched with Cl_2SbPh. The resulting product was isolated as a yellow solid in 67% yield and has been fully characterized by multinuclear NMR spectroscopy and combustion analysis. While stable under an atmosphere of nitrogen, **1** develops a pinkish coloration over time in ambient atmosphere and ^{1}H NMR spectroscopy evinces partial decomposition to the 2,2'-dibenzothiophene ligand. This observation has also been noted by Ohshita in their study of **F**-



Scheme 1. Synthesis of stiboranes **2** and **3**.

type compounds,[16] who characterized this as photodecomposition.Upon diffusion of pentane into a THF solution of **1**, we obtained crystals suitable for X-ray diffractometry allowing us to elucidate the solid-state structure of the compound (**Figure 2**). The Sb(III) center is embedded within the heteropentacene backbone and sits within the plane of the chromophore. The formation of this five-membered stibole ring results in a highly pyramidalized stibine center with its pendent phenyl group being nearly perpendicular to the plane of the chromophore. Similar to our other stibole systems,[2a, 7a] this geometry should allow for the mixing of the Sb-centered σ* orbital and the conjugated π system of the dibenzothiophene chromophore (**Figure 2**). Indeed, density functional theory (DFT) calculations of **1** reveal the significant contribution of the σ*(Sb-C) orbital to the LUMO (-1.751 eV), hinting that modulation of this orbital may have effects on the photophysical properties of the compound.

Oxidation of **1** was then accomplished *via* two routes depending upon the nature of the supporting ligand (**Scheme 1**). Firstly, **1** was treated with *o*-chloranil to afford dibenzothienostibaindole **2** which following purification by column chromatography yielded a yellow solid. Compared to **1**, the aromatic resonances of **2** are shifted downfield which clearly signal the increased oxidation state of the antimony center. Unlike the related catecholatophosporanes synthesized by Baumgartner and co-workers,[15] **2** is relatively tolerant to ambient conditions. Single crystals of the compound suitable for X-ray crystallography were obtained as yellow blocks *via* the diffusion

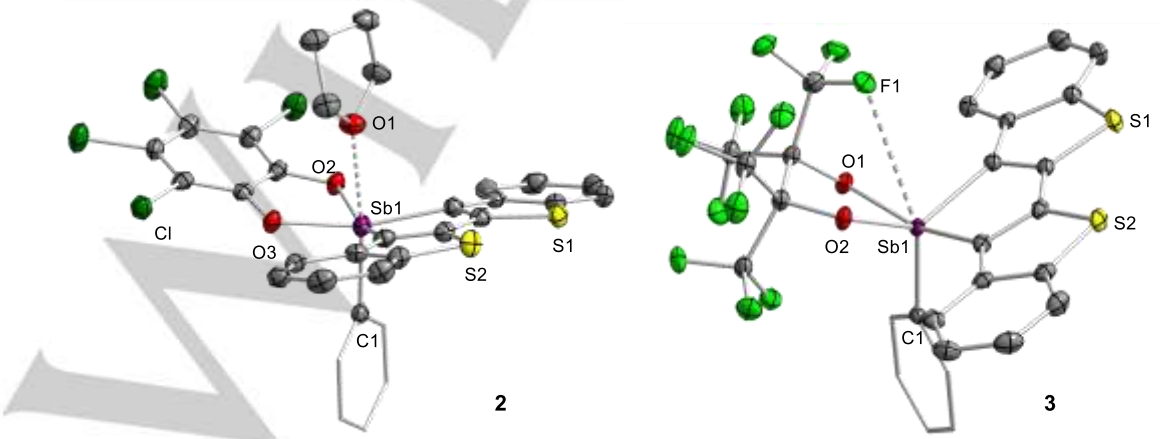


Figure 3. Solid-state structures of stiboranes **2** and **3**. Pertinent metrical information can be found in the main text.

of pentane vapors into a THF solution of the compound (**Figure 3**). Elucidation of the solid-state structure of **2** confirmed the identity of the resulting stiborane. Much like the rigid organic backbone of the previously reported catecholatostibaindoles, the planarity of the heteropentacene structure is retained upon oxidation. We were surprised to find that in the asymmetric unit, four distinct units of **2** crystallized each with a THF molecule coordinated to their antimony(V) center, leading to Sb-O_{THF} distances between 2.388(2) Å and 2.519(2) Å. These distances are longer than the Sb-O distances of related hydroxoantimonate anions[10] but are on par with Sb-O distances of other adducts bearing neutral oxygen donors.[12a, 19]

Compound **1** could also be oxidized following treatment with ^{t}BuOOH and was subsequently quenched with perfluoropinacol to afford the pinacolatostiborane **3** in 40% yield which was also crystallized for X-ray diffractometry (**Figure 3**). Compared to the solid-state structure of **2**, **3** also adopts a geometry that is intermediate between square pyramidal and trigonal bipyramidal as indicated by a τ_5[20] value of 0.43 though it does not accommodate an external Lewis base. While a wide range of τ_5 values has been observed previously for stiboranes,[21] stiboranes in which the central antimony atom is embedded in a heterocycle typically have τ_5 values lower than 0.5. That said, at the base of the square pyramid made by the stiborane is a fluorine atom of the trifluoromethyl group of the diol ligand at a short Sb-F_1 distance of 3.1834(14) Å that creates a F_1-Sb-C_1 vector of 154.09(5)°. This distance and this angle are comparable to those found for $(C_6F_5)_3Sb(o\text{-}O_2C_6Cl_4)$,[22] indicating a weak intramolecular donor-acceptor interaction or pnictogen bond,[23] as supported by NBO calculations (Figure S8). Altogether, these features suggest latent Lewis acidity at the antimony center of this pinacolatostiborane.

As we have previously shown, catecholatostiboranes are exemplary hard anion complexing agents,[7a, 10-11, 24] and we were thus curious to explore the Lewis acidic properties of **2** in particular. To begin, addition of TBAF to a CD_2Cl_2 solution of **2** visually appears to result in fluoride binding, producing an immediate color change from yellow to colorless. Indeed, a resonance in the ^{19}F NMR spectrum of that solution appears at -88.6 ppm (Figure S9), in the expected range from monodentate Sb(V)-F bonds. Finally, ESI mass spectrometry of the product solution reveals a monoanionic molecular ion peak at the expected mass for the fluoride adduct [**2**-F]$^-$ at *m*/*z* of 724.80. Addition of TBAF to a CD_2Cl_2 solution of **3** afforded a ^{19}F NMR spectrum that was more difficult to interpret than in the case of **2** (Figure S10). Also, ESI mass spectrometry only showed a weak peak for [**3**-F]$^-$ at *m*/*z* of 812.92. Given these uncertainties regarding the clean formation of [**3**-F]$^-$, we focused on **2,** which showed a less ambiguous behavior when combined with fluoride.

The spectroscopic change at λ = 420 nm induced upon addition of TBAF was monitored by UV-vis spectroscopy in CH_2Cl_2, which could be fitted to a 1:1 binding isotherm (**Figure 4**). This analysis found quantitative fluoride binding by **2**, with an association constant ($K(F^-)$) > 10^7 M^{-1}. DFT calculations were performed on **2** and the putative [**2**-F]$^-$ product revealed that the Sb-based σ* orbital is prominent in the low-lying LUMO of **2** (-2.492 eV) and is the likely source of Lewis acidity (**Figure 4**). Coordination of fluoride to Sb(V) engages this σ* orbital, leaving the LUMO with only π* contributions from the dithiophene ligand.

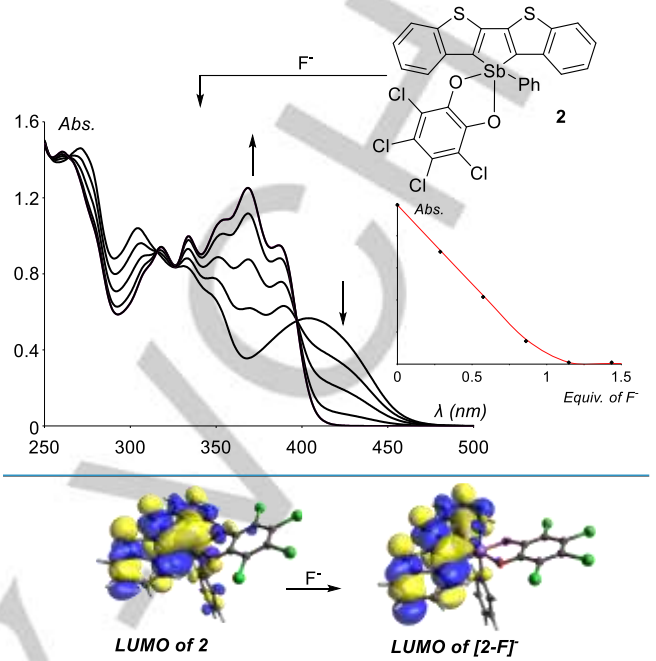


Figure 4. Top: UV-vis spectrum obtained by titration of **2** with TBAF in CH_2Cl_2. Binding isotherm constructed from absorption data at 420 nm is shown in the inset, with the experimental (black diamonds) and calculated (red line) 1:1 binding isotherm. The $K(F^-)$ was calculated to be > 10^7 M^{-1}. Bottom: Relevant DFT calculations of **2** and the putative [**2**-F]$^-$ demonstrating the role of the Sb in the fluoride binding process (LUMO isovalue: 0.02).

Conclusions

In summary, we report the synthesis of dibenzothienostibole **1** which can be oxidized to form the Lewis acidic Sb(V) compounds **2** and **3**. Fluoride binding at the Sb(V) center of **2** results in a colorimetric turn-off response from yellow to colorless. These results provide further confirmation that anion binding to the Sb-based σ* orbital directly influences the extent of π conjugation and, therefore, the photophysical properties of the surrounding chromophore.

Experimental Section

General considerations. 2,2'-di(3-bromobenzo[*b*]thiophene)[14] and Cl_2SbPh[25] were synthesized *via* literature procedures. . Et_2O was dried over Na/K and toluene was dried over Na. All other solvents used were ACS reagent grade and used as received. Elemental analyses were performed were performed at Atlantic Microlab (Norcross, GA). Absorbance measurements were taken on a Shimadzu UV-2502PC UV-Vis spectrophotometer against a solvent reference. NMR spectra were recorded at room temperature using a Varian Unity Inova 500 FT NMR spectrometer, a Bruker Avance 500 NMR spectrometer, or a Bruker 400 Ascend NMR spectrometer. Chemical shifts are given in ppm and are referenced against residual solvent signals (^{1}H, ^{13}C) or external C_6F_6 (-161.64 ppm

vs. $CFCl_3$ in $CDCl_3$, -162.61 ppm vs. $CFCl_3$ in CD_2Cl_2).[26] In the 1H and 13C NMR data, dibenzothiophene is referred to as dib and *o*-chloranil as chlo. Mass spectrometry was carried out by the Texas A&M Chemistry Mass Spectrometry Facility.

Synthesis of 1. 2,2'-di(3-bromobenzo[*b*]thiophene) (360 mg, 0.85 mmol) was dissolved in Et_2O (20 mL) and TMEDA (0.5 mL, mmol) and cooled to -78 °C. ^{n}BuLi (2.5 M in hexanes, 0.75 mL, 1.87 mmol) was then added dropwise, and the resulting suspension stirred at this reduced temperature for 10 min. Cl_2SbPh (343 mg, 1.27 mmol) was dissolved in Et_2O (10 mL) and the solution was added dropwise. The resulting yellow suspension was allowed to warm to room temperature and stir overnight. Solvent was removed *in vacuo*, and the yellow residue was resuspended in MeOH to precipitate a light yellow powder. Compound **1** was then isolated *via* column chromatography over silica gel (40:1 hexanes:CH_2Cl_2). Yield: 263 mg (67%, 0.57 mmol). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.84 Hz, 2H, dib C*H*), 7.84 (d, *J* = 7.90 Hz, 2H, dib C*H*), 7.52 (m, 2H, Sb*Ph*), 7.42 (td, *J* = 7.09 Hz & 1.05 Hz, 2H, dib C*H*), 7.39 (td, *J* = 7.19 Hz & 1.39 Hz, 2H, dib C*H*), 7.25 (m, 3H, Sb*Ph*). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.97 (s, dib *C*), 142.83 (s, dib *C* or Sb*Ph*), 142.36 (s, dib *C* or Sb*Ph*), 141.62 (s, Sb*Ph*), 137.00 (s, dib *C*), 135.58 (s, dib *C*), 129.35 (s, dib *C*), 129.18 (s, Sb*Ph*), 125.39 (s, dib *C*H), 124.56 (s, dib *C*H), 123.96 (s, dib *C*H), 123.32 (s, dib *C*H). Elemental analysis calculated for $C_{22}H_{13}S_2Sb$: C 57.04, H 2.83; found: C 57.00, H 2.72.

Synthesis of 2. *o*-Chloranil (98 mg, 0.40 mmol) in CH_2Cl_2 (1 mL) was added incrementally to a solution of **1** (135 mg, 0.30 mmol) in CH_2Cl_2 (5 mL). After stirring for 15 min, the solvent was removed *in vacuo*, and the residue was washed with MeOH on a frit. The bulk of the powder was transferred as a solid into a collection vial. The product remaining on the frit was washed down with CH_2Cl_2, generating a filtrate that was combined with the solid product in the collection vial. The collection vial was placed under vacuum affording **2** as a yellow solid. Yield: 160 mg (77%, 0.23 mmol). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.10 Hz, 2H, dib C*H*), 7.91 (d, *J* = 8.11 Hz, 2H, dib C*H*), 7.76 (m, 2H, Sb*Ph*), 7.56 (m, 3H, Sb*Ph*), 7.50-7.47 (m, 2H, dib C*H*), 7.45-7.41 (m, 2H, dib C*H*). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.37 (s, dib *C*), 144.49 (s, *o*-chloranil *C* or dib *C*), 143.13 (s, *o*-chloranil *C* or dib *C*), 139.78 (s, dib *C*), 133.94 (s, Sb*Ph*), 133.60 (s, Sb*Ph*), 130.78 (s, dib *C*), 130.64 (s, Sb*Ph*), 129.84 (s, dib *C*H), 126.83 (s, Sb*Ph*), 125.83 (s, dib *C*H), 125.40 (s, dib *C*H), 123.33 (s, dib *C*H), 121.92 (s, *o*-chloranil *C*), 117.50 (s, *o*-chloranil *C*). Elemental analysis calculated for $C_{28}H_{13}Cl_4O_2S_2Sb$ + 0.3 (CH_2Cl_2): C 46.27, H 1.87; found: C 45.94, H 1.63 (^{1}H NMR indicates the presence of ~0.3 equiv. of CH_2Cl_2). ESI-MS calculated for $[C_{28}H_{14}Cl_4O_2S_2Sb]^+$ 710.8196, found 710.8170.

Synthesis of 3. Under an atmosphere of N_2, **1** (225 mg, 0.50 mmol) and perfluoropinacol (236 mg, 0.70 mmol) were dissolved in toluene (10 mL), to which a solution of ^{t}BuOOH (96 mg, 0.75 mmol) in toluene (1 mL) was added dropwise at 0 °C. The mixture was stirred for overnight, and then solvent was removed *in vacuo*. After washing with MeOH, compound **3** was isolated as a yellow powder. Yield: 157 mg (40%, 0.20 mmol). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.9 Hz, 2H, dib C*H*), 7.91-7.90 (dd, *J* = 0.8 Hz & 8.2 Hz, 2H, dib C*H*), 7.81-7.82 (m, 2H, Sb*Ph*), 7.54 (m, 3H, Sb*Ph*), 7.47 (t, *J* = 7.52 Hz, 2H, dib C*H*), 7.44-7.41 (t, *J* = 7.58 Hz, 2H, dib C*H*). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.86 (s, dib *C*), 143.13 (s, dib *C*), 139.68 (s, dib *C*), 134.34 (s, Sb*Ph*), 133.44 (s, Sb*Ph*), 130.80 (s, Sb*Ph*), 130.31 (s, dib *C*H), 129.45 (s, dib *C*), 126.71 (s, dib *C*H), 125.78 (s, Sb*Ph*), 124.99 (s, dib *C*H), 123.29 (s, dib *C*H), 122.41 (q, *J* = 292.64 Hz, *C*F_3), 79.52 (broad s, *C*$(CF_3)_2$). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -69.28. Elemental analysis calculated for $C_{28}H_{13}F_{12}O_2S_2Sb$: C 42.29, H 1.65; found: C 42.34, H 1.63. ESI-MS calculated for $[C_{28}H_{14}F_{12}O_2S_2Sb]^+$ 796.9280, found 796.9276.

Crystallography. Crystallographic measurements were performed at 110(2) K or 296 K using a Bruker APEX-II CCD area diffractometer with a graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). Single crystals of **1**, **2**-THF, and **3** were obtained *via* diffusion of pentane into a THF solution of the compound. In each case, a specimen of suitable size and qualty was selected an mounted onto a nylon loop. The semi-empirical method SADABS[27] was applied for absorption correction. The structure was solved by direct methods using SHELXT[28] and refined by the full-matrix least square technique against F^2 with the anisotropic temperature parameters for all non-hydrogen atoms. All H atoms were geometrically placed and refined in a riding model approximation. Data reduction and further calculations were performed using ShelXL.[29] Diamond4 was used for final data presentation. CCDC 2386475-2386477 contains the supplementary crystallographic data for this work. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax:+44 1223 336033.

DFT calcuations. Geometry optimizations were performed using the Gaussian 16[30] program. In all cases, the structures were optimized using the B3LYP functional[31] and the following mixed bassis sets: aug-cc-pVTZ-PP (Sb),[32] 6-311G(d) (S/Cl),[33] 6-31G(d') (F),[32] 6-31G(d) (C/H/O).[34] When available, the experimentally determined geometry of the derivative was used as an initial guess for the optimization. Frequency calculations were carried out to confirm the absence of imaginary frequencies. NBO calculations were performed using NBO 7.0[35] at the same level of theory. The molecular orbitals and NBOs were visualized using Avogadro.

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Keywords: antimony • fluoride • Lewis acid • oxidation • chromophore

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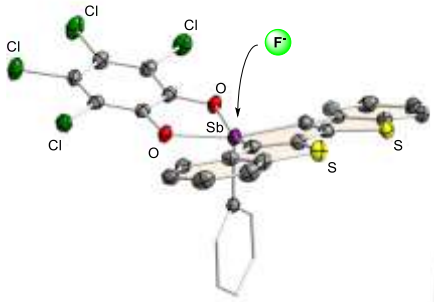
ARTICLE

FULL PAPER

A stiborane, obtained by addition of *o*-chloranil to a dibenzothienostibole has been synthesized and employed as a Lewis acid for the complexation of the fluoride anion.



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TitleFluoride binding by a neutral organoantimony(V) Lewis acid embedded within a dibenzodithiophene chromophore