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Synthesis and Properties of a Cationic Bidentate Lewis Acid

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As part of our efforts to increase the fluoride affinity of bidentate Lewis acids, we have set out to determine if the F^- anion chelation occurring in such systems can be complemented by favorable Coulombic attractions. To explore this idea, the neutral B/Hg bidentate Lewis acid 1-$\{Mes_2B\}$-8-$\{(2,6\text{-}Me_2\text{-}4\text{-}Me_2NC_6H_2)Hg\}C_{10}H_6$ (**3**) and its cationic analogue $[1\text{-}\{Mes_2B\}\text{-}8\text{-}\{(2,6\text{-}Me_2\text{-}4\text{-}Me_3NC_6H_2)Hg\}C_{10}H_6]^+$ ([**4**]$^+$) have been synthesized and studied. Compound **3** as well as the triflate salt of [**4**]$^+$ react with $[S(NMe_2)_3][Me_3SiF_2]$ to afford the corresponding fluoride complexes [**3**-μ_2-F]$^-$ and [**4**-μ_2-F]. Spectroscopic and structural studies confirm that the F^- anion bridges the two Lewis acidic centers in both [**3**-μ_2-F]$^-$ and [**4**-μ_2-F]. UV–vis titration experiments carried out in tetrahydrofuran/water (9/1, v/v) mixtures indicate that the fluoride binding constants of **3** and [**4**]$^+$ are clearly differentiated and are equal to 1.3 ($\pm$0.1) $\times$ 10^2 M^{-1} and 6.2 ($\pm$0.2) $\times$ 10^4 M^{-1}, respectively. The enhanced fluoride binding constant of [**4**]$^+$, when compared to **3**, confirms that the chelate effect occurring in these types of fluoride receptors can be combined with favorable Coulombic attractions to strengthen the host–guest interaction. Cation [**4**]$^+$ remains highly selective for F^- over other environmentally abundant anions including Cl^-, Br^-, NO_3^-, $H_2PO_4^-$, and HSO_4^- and shows only a weak response to OAc^-. Finally, the addition of an aqueous solution of Al^{3+} to a solution containing [**4**-μ_2-F] leads to complete regeneration of [**4**]$^+$, showing that F^- binding is reversible.

Introduction

The ion recognition of fluoride in aqueous media is attracting a great deal of interest because of the importance of this anion in the areas of health and defense. A plethora of organic hosts that interact with the anionic guests via hydrogen bonds have been reported.[1] Unfortunately, these receptors are typically incompetent in aqueous environments where water interferes with the host–guest interactions.[2] Because of these complications, fluorophilic Lewis acidic derivatives[3,4] including boronic acids, boronic esters, and neutral boranes are receiving increasing attention.[5] Neutral triarylboranes, for example, complex F^- anions to form the corresponding triarylfluoroborate anions.[6] While this property has long been overlooked in the context of anion sensing, Yamaguchi et al. showed that such boranes can serve as fluoride sensors with binding constants ranging from 10^5 to 10^6 M^{-1} in organic solvents.[7,8] Since these seminal contributions, a number of other groups have reported related

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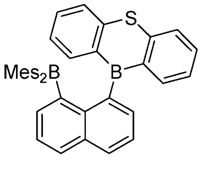
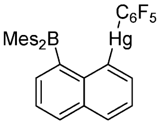
results.[9,10] However, despite the elevated binding constants and advantageous photophysical properties, triarylboranes are unable to overcome the large hydration enthalpy of the F^- anion and cannot be used in water.[8]

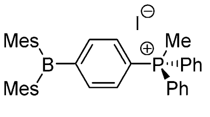
In order to increase the binding constants of borane-based receptors, several groups, including ours, have explored the use of bidentate boranes that chelate F^-.[9,11−13] Our efforts in this area have focused on the design of naphthalene-based derivatives such as **I**.[9] Although the fluoride binding constants of such receptors exceed those of monofunctional analogues by 3 or 4 orders of magnitude, these compounds cannot be used in water because they slowly hydrolyze.[9] Such limitations do not seem to affect the heteronuclear B/Hg bidentate Lewis acid **II**, which captures F^- in tetrahydrofuran (THF)/water mixtures without decomposition.[13] In addition to investigating derivatives whose fluoride affinity is increased by the chelating properties of the receptor, several groups, including ours, are studying the use of cationic boranes.[14,15] The initial results obtained in this area indicate that the fluoride affinity of such receptors is greatly increased by Coulombic effects. For example, the phosphonium borane [**III**]$^+$, unlike any of its neutral analogues, captures F^- in aqueous solution.[15] In principle, a further increase in the fluoride affinity of B-based receptors could be obtained if the chelate effect occurring in a bidentate Lewis acid was complemented by favorable Coulombic attractions. In an effort to validate this hypothesis, we have synthesized a cationic B/Hg bidentate Lewis acid and compared its fluoride affinity to that of its neutral precursor.



I



II



[III][I]

Experimental Section

General Considerations. ***Caution!*** *Because of the toxicity of the mercury compounds discussed in these studies, great care should be exercised when synthesizing and handling compounds.* Tetrakis(tetrahydrofuran)lithium dimesityl-1,8-naphthalenediylborate (**1**) was synthesized by the published procedures.[16,17] Methyl triflate (MeOTf) and $[S(NMe_2)_3][Me_3SiF_2]$ (TASF) were purchased from Aldrich, $Hg(OAc)_2$ was purchased from Fisher Scientific, 3,5,*N*,*N*-tetramethylaniline and n-$Bu_4NF{\cdot}3H_2O$ (TBAF) from Alfa Aesar were purchased, and all were used as received. Solvents were dried by passing them through an alumina column (*n*-hexane and CH_2Cl_2) or by reflux under N_2 over Na/K (Et_2O and THF). Air-sensitive compounds were handled under a N_2 atmosphere using standard Schlenk and glovebox techniques. UV−vis spectra were recorded on a HP8453 spectrophotometer. Elemental analyses were performed at Atlantic Microlab (Norcross, GA). NMR spectra were recorded on Varian Inova 400 FT NMR spectrometer (399.59 MHz for ^1H, 375.99 MHz for ^{19}F, 128.02 MHz for ^{11}B, 100.48 MHz for ^{13}C, and 71.57 MHz for ^{199}Hg) at ambient temperature. Chemical shifts are given in ppm and are referenced against external Me_4Si (^1H, ^{13}C), $BF_3{\cdot}Et_2O$ (^{11}B), $CFCl_3$ (^{19}F), and $HgMe_2$ (^{199}Hg).

Crystallography. The crystallographic measurement was performed using a Bruker Apex II-CCD area detector diffractometer, with a graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å). A specimen of suitable size and quality was selected and mounted onto a glass fiber with apiezon grease. The structure was solved by direct methods, which successfully located most of the non-H atoms. Subsequent refinement on F^2 using the *SHELXTL/PC* package (version 5.1) allowed the location of the remaining non-H atoms. In the case of [**4**-μ_2-F]MeCN, the largest residual peak of 2.487 e Å^{-3} is located at 0.935 Å from the Hg2 atom and most likely results from absorption.

Synthesis of $(2,6\text{-}Me_2\text{-}4\text{-}Me_2NC_6H_2)HgCl$ (2). 3,5,*N*,*N*-Tetramethylaniline (10 mmol, 1.49 g) was added to a slurry of $Hg(OAc)_2$ (10 mmol, 3.19 g) in EtOH (15 mL) at room temperature. After it was stirred for 6 h, the mixture was filtered and washed with EtOH. The resulting white solid was dissolved in warm acetone (20 mL), and EtOH (10 mL) was added to the solution. Next, the solution was treated with a saturated aqueous solution of LiCl (20 mL), which resulted in the formation of a white precipitate. After 30 min of stirring, the precipitate was isolated by filtration and successively washed with water and *n*-hexane. Drying in vacuo at 50 °C overnight afforded **2** as a white powder (3.11 g, 81%). ^1H NMR ($CDCl_3$): δ 2.41 (s, 6H, Ar−CH_3), 2.94 (s, 6H, NCH_3), 6.45 (s, 2H, Ar−H). ^{13}C NMR ($CDCl_3$): δ 26.71 (Ar−CH_3), 40.26 (NCH_3), 110.89 (Ar−C3), 140.45 (Ar−C1), 142.63 (Ar−C2), 151.31 (Ar−C4). ^{199}Hg NMR ($CDCl_3$): δ −984.3. Anal. Calcd for $C_{10}H_{14}ClHgN$: C, 31.26; H, 3.67. Found: C, 30.98; H, 3.55.

Synthesis of 1-{Mes_2B}-8-{$(2,6\text{-}Me_2\text{-}4\text{-}Me_2NC_6H_2)Hg$}$C_{10}H_6$ (3). To the solid mixture of **1** (500 mg, 0.745 mmol) and **2** (286 mg, 0.745 mmol) was added cold (−20 °C) THF (10 mL). After it was stirred overnight at room temperature, the solvent was removed under reduced pressure and the residue was extracted with *n*-hexane (30 mL). Following filtration and evaporation of the solvent, the light-yellow solid was washed with acetonitrile (3 × 4 mL) and dried under vacuum to yield an ivory powder (378 mg, 70%). ^1H NMR ($CDCl_3$): δ 1.29 (s, 3H, Mes−CH_3), 1.70 (s, 3H, Mes−CH_3), 1.74 (s, 3H, Mes−CH_3), 2.10 (s, 6H, Ar−CH_3), 2.19 (s, 3H, Mes−CH_3), 2.29 (s, 3H, Mes−CH_3), 2.37 (s, 3H, Mes−CH_3), 2.91

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(s, 6H, NCH_3), 6.42 (br s, 1H, Mes−C*H*), 6.46 (s, 2H, Ar−*H*), 6.61 (br s, 1H, Mes−C*H*), 6.74 (br s, 1H, Mes−C*H*), 6.81 (br s, 1H, Mes−C*H*), 7.35−7.38 (m, 2H, Naph−C*H*), 7.43 (dd, 1H, $^3J_{\mathrm{H-H}}$ = 7.2 Hz, $^4J_{\mathrm{H-H}}$ = 1.6 Hz, Naph−C*H*), 7.55 (dd, 1H, $^3J_{\mathrm{H-H}}$ = 8.0 Hz, $^4J_{\mathrm{H-H}}$ = 6.8 Hz, Naph−C*H*), 7.78 (dd, 1H, $^3J_{\mathrm{H-H}}$ = 8.2 Hz, $^4J_{\mathrm{H-H}}$ = 1.6 Hz, Naph−C*H*), 7.95 (dd, 1H, $^3J_{\mathrm{H-H}}$ = 8.0 Hz, $^4J_{\mathrm{H-H}}$ = 1.6 Hz, Naph−C*H*). ^{13}C NMR (CDCl$_3$): δ 21.25 (Ar−*C*H$_3$), 22.36, 23.51, 24.68, 25.26, 25.55 (Mes−*C*H$_3$), 57.62 (N*C*H$_3$), 111.67, 125.21, 125.35, 127.61, 128.14, 129.18, 129.56, 130.07, 133.52, 134.28, 134.72, 136.47, 138.21, 139.55, 139.97, 140.51, 141.30, 142.40, 143.76, 144.66, 145.43, 146.68, 150.33, 152.91, 157.35, 176.51. ^{11}B NMR (CDCl$_3$): δ +72.1. ^{199}Hg NMR (CDCl$_3$): δ −584.6. UV−vis (THF): λ_{max}/nm (log ϵ) 363 (4.04). Anal. Calcd for $C_{38}H_{42}BHgN$: C, 63.03; H, 5.85. Found: C, 62.91; H, 5.97.

Synthesis of [S(NMe$_2$)$_3$][1-{Mes$_2$B}-(μ_2-F)-8-{(2,6-Me$_2$-4-Me$_2$NC$_6$H$_2$)Hg}C$_{10}$H$_6$] ([S(NMe$_2$)$_3$][3-μ_2-F]). To a solid mixture of **3** (20 mg, 0.028 mmol) and TASF (7.7 mg, 0.028 mmol) was added CH$_2$Cl$_2$ (2 mL) at room temperature. The reaction mixture was stirred for 30 min, layered with *n*-hexane, and stored at −20 °C to induce the crystallization of [S(NMe$_2$)$_3$][**3**-μ_2-F]. After filtration and washing with ether (2 × 1 mL), the product was obtained as colorless crystals (18 mg, 71%). ^{1}H NMR (acetone-*d*$_6$): δ 1.68 (br s, 9H, Mes−CH_3), 2.06 (br s, 9H, Mes−CH_3), 2.12 (s, 6H, Ar−CH_3), 2.82 (s, 6H, NCH_3), 3.00 (s, 18H, S(N*Me*$_2$)), 6.32 (br s, 4H, Mes−C*H*), 6.36 (s, 2H, Ar−*H*), 6.99 (t, 1H, $^3J_{\mathrm{H-H}}$ = 7.2 Hz, Naph−C*H*), 7.21 (d, 2H, $^3J_{\mathrm{H-H}}$ = 5.6 Hz, Naph−C*H*), 7.30 (dd, 1H, $^3J_{\mathrm{H-H}}$ = 6.8 Hz, $^4J_{\mathrm{H-H}}$ = 1.2 Hz, Naph−C*H*), 7.46 (dd, 1H, $^3J_{\mathrm{H-H}}$ = 8.0 Hz, $^4J_{\mathrm{H-H}}$ = 1.6 Hz, Naph−C*H*), 7.54 (t, 1H, $^3J_{\mathrm{H-H}}$ = 4.8 Hz, Naph−C*H*). ^{13}C NMR (acetone-*d*$_6$): δ 21.12 (Ar−*C*H$_3$), 25.21 (br s, Mes−*C*H$_3$), 25.79, 25.81 (Mes−*C*H$_3$), 38.65 (S(N*Me*$_2$)), 41.08 (N*C*H$_3$), 111.98, 123.17, 125.12, 126.96, 128.93, 129.04 (br), 132.75, 132.81, 136.08, 136.12, 136.45, 145.32, 147.94, 147.98, 150.46, 158.60, 178.92, 179.03. ^{19}F NMR (acetone-*d*$_6$): δ −165.1. ^{11}B NMR (acetone-*d*$_6$): δ +8.7. ^{199}Hg NMR (acetone-*d*$_6$): δ −708.6 (d, $^1J_{\mathrm{Hg-F}}$ = 109.8 Hz). Anal. Calcd for $C_{44}H_{60}BFHgN_4S$: C, 58.24; H, 6.66. Found: C, 57.98; H, 6.76.

Synthesis of [1-{Mes$_2$B}-8-{(2,6-Me$_2$-4-Me$_3$NC$_6$H$_2$)Hg}C$_{10}$H$_6$]-[OTf] (4[OTf]). An excess of MeOTf (0.1 mL) was slowly added to a CH$_2$Cl$_2$ solution (5 mL) of **3** (200 mg, 0.276 mmol) at room temperature. Within a few minutes, a white solid began to precipitate. After stirring for 2 h, the solid was isolated by filtration and washed twice with Et$_2$O (2 × 10 mL). Drying under vacuum afforded [**4**][OTf] as a white powder (231 mg, 94%). Colorless single crystals could be obtained by slow evaporation of a methanol solution of [**4**][OTf]. ^{1}H NMR (DMSO-*d*$_6$): δ 1.23 (s, 3H, Mes−CH_3), 1.50 (s, 3H, Mes−CH_3), 1.65 (s, 3H, Mes−CH_3), 2.18 (s, 6H, Ar−CH_3), 2.21 (br s, 6H, Mes−CH_3), 2.31 (s, 3H, Mes−CH_3), 3.57 (s, 9H, NCH_3), 6.31 (br s, 1H, Mes−C*H*), 6.74 (br s, 2H, Mes−C*H*), 6.83 (br s, 1H, Mes−C*H*), 7.31 (d, 1H, $^3J_{\mathrm{H-H}}$ = 6.8 Hz, Naph−C*H*), 7.45 (t, 1H, $^3J_{\mathrm{H-H}}$ = 7.6 Hz, Naph−C*H*), 7.57 (s, 2H, Ar−*H*), 7.60 (t, 1H, $^3J_{\mathrm{H-H}}$ = 7.2 Hz, Naph−C*H*), 7.65 (d, 1H, $^3J_{\mathrm{H-H}}$ = 6.0 Hz, Naph−C*H*), 7.91 (d, 1H, $^3J_{\mathrm{H-H}}$ = 7.6 Hz, Naph−C*H*), 8.08 (d, 1H, $^3J_{\mathrm{H-H}}$ = 8.4 Hz, Naph−C*H*). ^{1}H NMR (acetone-*d*$_6$): δ 1.39 (s, 3H, Mes−CH_3), 1.59 (s, 3H, Mes−CH_3), 1.73 (s, 3H, Mes−CH_3), 2.22 (br s, 6H, Mes−CH_3), 2.28 (s, 6H, Ar−CH_3), 2.36 (s, 3H, Mes−CH_3), 3.86 (s, 9H, NCH_3), 6.34 (br s, 1H, Mes−C*H*), 6.77 (br s, 2H, Mes−C*H*), 6.85 (br s, 1H, Mes−C*H*), 7.42−7.49 (m, 2H, Naph−C*H*), 7.59−7.64 (m, 2H, Naph−C*H*), 7.74 (s, 2H, Ar−*H*), 7.93 (dd, 1H, $^3J_{\mathrm{H-H}}$ = 7.2 Hz, $^4J_{\mathrm{H-H}}$ = 2.8 Hz, Naph−C*H*), 8.11 (dd, 1H, $^3J_{\mathrm{H-H}}$ = 7.6 Hz, $^4J_{\mathrm{H-H}}$ = 1.6 Hz, Naph−C*H*). ^{13}C NMR (DMSO-*d*$_6$): δ 20.88 (Ar−*C*H$_3$), 21.90, 23.05, 24.22, 24.89 (Mes−*C*H$_3$), 56.30 (N*C*H$_3$), 117.34, 125.16, 125.65, 127.63, 128.19, 129.47, 129.75, 129.86, 133.80, 133.83, 134.37, 137.57, 137.93, 138.61, 139.04, 139.91, 141.51, 142.03, 143.08, 144.31, 145.45, 146.34, 146.68, 152.13, 171.96, 173.46. ^{199}Hg NMR (DMSO-*d*$_6$): δ −693.9. UV−vis (THF): λ_{max}/nm (log ϵ) 362 (4.01). Anal. Calcd for $C_{40}H_{45}BF_3HgNO_3S$: C, 54.09; H, 5.11. Found: C, 54.27; H, 5.16.

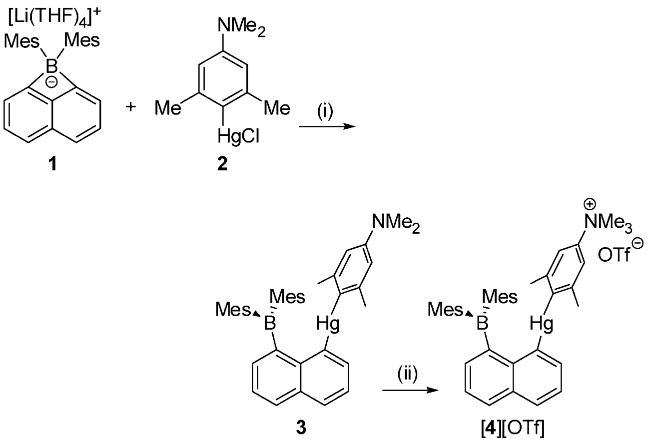
Synthesis of 1-{Mes$_2$B}-(μ_2-F)-8-{(2,6-Me$_2$-4-Me$_3$NC$_6$H$_2$)Hg}-C$_{10}$H$_6$ ([4-μ_2-F]). TASF (21 mg, 0.076 mmol) was added to a slurry of [**4**][OTf] (60 mg, 0.068 mmol) in CH$_2$Cl$_2$ (2 mL) at room temperature. Shortly after the addition was complete, the reaction mixture turned into a homogeneous solution. Further stirring for 2 h led to the formation of a precipitate, which was isolated by filtration and washed with cold CH$_2$Cl$_2$ (2 × 1 mL). Drying in vacuo afforded [**4**-μ_2-F] as a white powder (32 mg, 62%). Single crystals of [**4**-μ_2-F] were obtained by slow evaporation of an acetonitrile solution. ^{1}H NMR (acetone-*d*$_6$): δ 1.63 (br s, 9H, Mes−CH_3), 2.06 (br s, 9H, Mes−CH_3), 2.28 (s, 6H, Ar−CH_3), 3.79 (s, 9H, NCH_3), 5.89 (br s, 1H, Mes−C*H*), 6.36 (br s, 2H, Mes−C*H*), 6.54 (br s, 1H, Mes−C*H*), 7.02 (t, 1H, $^3J_{\mathrm{H-H}}$ = 7.2 Hz, Naph−C*H*), 7.23−7.26 (m, 2H, Naph−C*H*), 7.31 (d, 1H, $^3J_{\mathrm{H-H}}$ = 6.8 Hz, Naph−C*H*), 7.45 (s, 2H, Ar−*H*), 7.50 (d, 1H, $^3J_{\mathrm{H-H}}$ = 8.0 Hz, Naph−C*H*), 7.60 (dd, 1H, $^3J_{\mathrm{H-H}}$ = 6.8 Hz, $^4J_{\mathrm{H-H}}$ = 2.4 Hz, Naph−C*H*). ^{13}C NMR (acetone-*d*$_6$): δ 21.11 (Ar−*C*H$_3$), 24.61, 25.11, 25.59, 25.62 (Mes−*C*H$_3$), 57.62 (N*C*H$_3$), 116.30, 123.23, 125.33, 127.11, 128.42 (br), 129.00 (br), 129.50 (br), 131.62, 133.19, 133.25, 136.19, 136.22, 136.44, 141.25, 143.30, 146.51, 147.43, 147.47, 147.72, 152.15 (br), 157.17 (br), 161.95 (br), 174.26, 174.36, 175.73. ^{19}F NMR (acetone-*d*$_6$): δ −164.7. ^{11}B NMR (acetone-*d*$_6$): δ +8.9. ^{199}Hg NMR (acetone-*d*$_6$): δ −759.8 (d, $^1J_{\mathrm{Hg-F}}$ = 122.0 Hz). Anal. Calcd for $C_{39}H_{45}BFHgN$: C, 61.78; H, 5.98. Found: C, 61.78; H, 6.01.

UV−Vis Titrations in THF. A THF solution of **3** or [**4**][OTf] (5×10^{-5} M, 3.0 mL) was titrated with incremental amounts of F$^-$ anions by the addition of a solution of TBAF in THF (3.69×10^{-3} M). The absorption was monitored at λ_{max} = 363 nm (ϵ = 10 900) for **3** and at λ_{max} = 362 nm (ϵ = 10 100) for [**4**][OTf]. The experimental data obtained were fitted to a 1:1 binding isotherm.

UV−Vis Titrations in THF/H$_2$O. A THF/H$_2$O (9/1, v/v) solution of **3** or [**4**][OTf] (4.5×10^{-5} M, 3.0 mL) was titrated with incremental amounts of F$^-$ anions by the addition of a solution of TBAF in THF (1.07×10^{-1} M for **3** and 6.66×10^{-3} M for [**4**]-[OTf]). The absorption was monitored at λ_{max} = 361 nm (ϵ = 10 300) for **3** and at λ_{max} = 363 nm (ϵ = 9870) for [**4**][OTf]. The experimental data obtained were fitted to a 1:1 binding isotherm. In order to confirm that fluoride complexation by [**4**]$^+$ is reversible, the following experiment was carried out. To a solution of [**4**][OTf] [3.0 mL, 4.5×10^{-5} M; THF/H$_2$O (9/1, v/v)] was added 5 μL of TBAF in THF (6.75×10^{-2} M). After the system had reached equilibrium, aliquots of an aqueous solution of AlCl$_3$ (0.01 M, 2 → 10 μL) were added incrementally and the absorption was recorded after each addition.

Theoretical Calculations. Density functional theory (DFT) calculations (full geometry optimization) were carried out with *Gaussian 03*[18] using the BP86 functional with the following basis sets: 6-31g for all C and H atoms,[19] 6-31+g(d′) for the B and N atoms,[20] and Stuttgart RSC 1997 ECP for the Hg centers.[21] Frequency calculations, which were carried out on the optimized structure of each compound, confirmed the absence of imaginary frequencies. Frontier orbitals were obtained from the optimized geometry.

Scheme 1[a]



[a] (i) THF, 25 °C, 70%. (ii) MeOTf, CH_2Cl_2, 25 °C, 94%.

Results and Discussion

Synthesis and Characterization. Reaction of **1**[16] with **2**, which was obtained by mercuration of *N*,*N*,3,5-tetramethylaniline,[22] afforded the neutral heteronuclear Lewis acid **3** as an ivory solid in 70% yield (Scheme 1). This new derivative reacts with MeOTf to afford the ammonium triflate salt [**4**][OTf]. Both **3** and [**4**][OTf] are air- and water-stable. While **3** dissolves in common organic solvents, solubilization of [**4**][OTf] requires polar solvents such as acetone or dimethyl sulfoxide (DMSO). The identities of **3** and [**4**][OTf] have been confirmed by multinuclear NMR spectroscopy and elemental analysis. In both cases, the ^{1}H NMR spectrum exhibits six distinct resonances that correspond to the aromatic CH groups of the unsymmetrically substituted naphthalene backbone. Four aryl and six methyl proton resonances are observed for the two mesityl groups, thus indicating the existence of a congested structure. The proton resonances of the dimethylamino group in **3** and the trimethylammonium group in [**4**][OTf] appear at 2.91 ppm ($CDCl_3$) and 3.57 ppm (DMSO-d_6), respectively. The ^{11}B NMR signal detected at 72.1 ppm for **3** is comparable to that of **II** and confirms the presence of a base-free trigonal-planar B center.[13] In the case of [**4**][OTf], the ^{11}B NMR resonance could not be detected despite extended acquisition times. The ^{199}Hg NMR signals of **3** and [**4**][OTf] are observed at −584.6 and −693.9 ppm, respectively, and are both in the expected range for a diarylmercurial.[23] The ^{199}Hg NMR chemical shift of [**4**][OTf] is close to that of **II** (−741.9 ppm). In THF, the UV spectra of **3** and [**4**][OTf] feature a broad absorption band at 363 nm ($\epsilon_{363} = 10\,100$) for **3** and 362 nm ($\epsilon_{362} = 10\,100$) for [**4**][OTf]. These bands are clearly red-shifted when compared to the absorption of naphthalene ($\lambda_{max} = 286$ nm) and confirm the presence of a three-coordinate B center, which mediates conjugation of the naphthalenediyl and mesityl substituents.[13]

Single crystals of [**4**][OTf] have been analyzed by X-ray diffraction. These crystals belong to the monoclinic space group $P2_1/c$ (Figure 1 and Table 1). The B1 atom adopts a trigonal-planar geometry ($\Sigma_{C-B-C} = 359.2°$) and is separated from the Hg1 atom by only 3.328(4) Å, which is very similar to the B−Hg distance observed in **II**.[13] The B1−C1−C9 [128.6(3)°] and Hg1−C8−C9 [130.4(3)°] angles substantially deviate from the ideal value of 120° and indicate the existence of a crowded structure. The short C20−Hg1 distance of 3.022(4) Å indicates the presence of a secondary Hg−π interaction involving the *ipso*-C atom of one of the mesityl groups. This Hg−π interaction leads to a noticeable deviation of the C8−Hg1−C29 angle [167.7(2)°] from linearity. Such an interaction has been observed in **II**[13] and is reminiscent of the B−π interactions sometimes observed in 1,8-diborylnaphthalenes.[24]

Compounds **3** and [**4**][OTf] can be converted into their respective fluoride complexes [$S(NMe_2)_3$][**3**-μ_2-F] and [**4**-μ_2-F] by reaction with TASF in CH_2Cl_2 (Scheme 2). The chelation of the F^- anion in both complexes is supported by their NMR spectroscopic features, which are very similar to those of [**II**-μ_2-F]$^-$ (Table 2). Some of the salient features include the following: the ^{11}B NMR signal, which clearly indicates the presence of a four-coordinate B center; the ^{19}F NMR signal, which is close to that observed in other fluoride-bridged species;[9,12,13] the detection of a doublet in the ^{199}Hg NMR spectrum, confirming the presence of a Hg−F linkage. The difference observed in $^{1}J_{Hg-F}$ for [**3**-μ_2-F]$^-$ and [**4**-μ_2-F] suggests that the Hg center of [**4**]$^+$ is more fluorophilic than that of **3**.

Crystals of [**4**-μ_2-F] can be obtained from CH_3CN. These crystals belong to the monoclinic space group $P2_1/c$ (Table 1). The asymmetric unit contains two independent molecules, denoted as **A** and **B**, which have very similar structures (Figure 1). The B−F bond lengths of 1.474(8) Å (**A**) and 1.488(8) Å (**B**) are comparable to those found in triarylfluoroborates.[8,15] The Hg−F bonds of 2.618(3) Å (**A**) and 2.646(4) Å (**B**) correspond to strong secondary interactions that are well within the sum of the van der Waals radii of Hg (1.75 Å)[25] and F (1.30−1.38 Å).[26] These Hg−F distances

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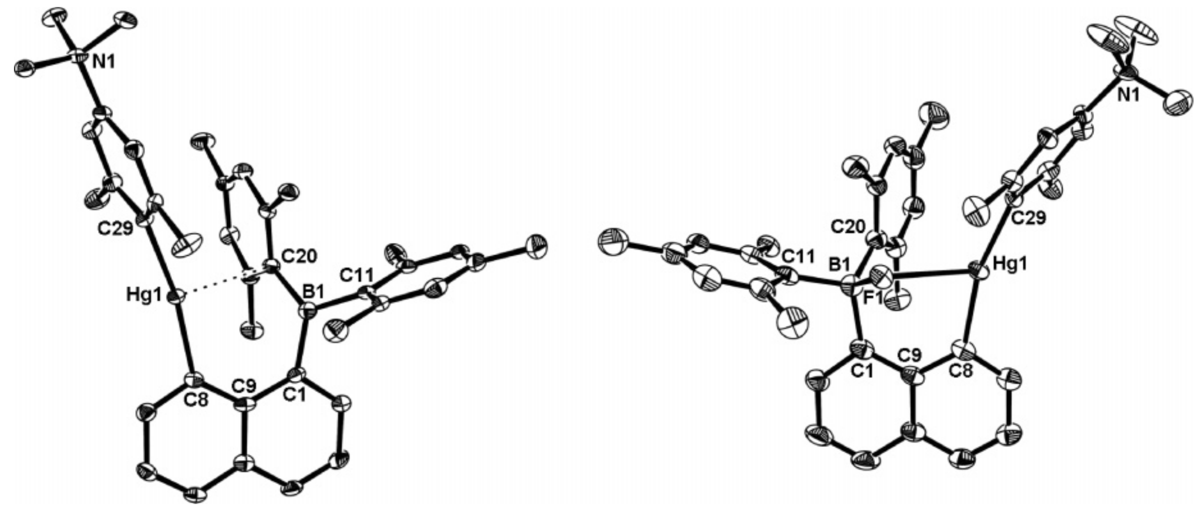

Figure 1. Crystal structures of $[\mathbf{4}]^+$ in [**4**][OTf] and [**4**-μ_2-F] (50% ellipsoid). For [**4**-μ_2-F], only molecule **A** is shown. H atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows. $[\mathbf{4}]^+$: B1−C1 1.576(6), B1−C11 1.582(6), B1−C20 1.570(6), Hg1−C8 2.084(4), Hg1−C29 2.092(4); C1−B1−C11 115.3(3), C1−B1−C20 125.1(3), C11−B1−C20 118.8(3), B1−C1−C9 128.6(3), Hg1−C8−C9 130.4(3), C8−Hg1−C29 167.7(2). [**4**-μ_2-F] [the metrical parameters of the second independent molecule (**B**) are provided in brackets]: B1−C1 1.654(8) [1.667(10)], B1−C11 1.656(8) [1.663(10)], B1−C20 1.679(9) [1.669(10)], B1−F1 1.474(8) [1.488(8)], Hg1−F1 2.618(3) [2.646(4)], Hg1−C8 2.092(6) [2.079(6)], Hg1−C29 2.093(6) [2.086(6)]; C1−B1−C11 110.3(5) [109.7(5)], C1−B1−C20 119.2(5) [119.0(6)], C11−B1−C20 109.0(5) [112.2(5)], B1−C1−C9 125.1(5) [126.1(6)], Hg1−C8−C9 129.0(4) [127.5(5)], C8−Hg1−C29 162.2(2) [164.1(2)], B1−F1−Hg1 98.2(3) [96.8(3)].

Table 1. Crystal Data, Data Collection, and Structure Refinement for [**4**][OTf] and [**4**-μ_2-F]

	[**4**][OTf]	[**4**-μ_2-F]•MeCN
	Crystal Data	
formula	$C_{40}H_{45}BF_3HgNO_3S$	$C_{41}H_{48}BFHgN_2$
M_r	888.23	799.21
cryst size (mm^3)	0.24 × 0.12 × 0.05	0.40 × 0.15 × 0.05
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	25.412(5)	23.700(5)
b (Å)	13.069(3)	11.660(2)
c (Å)	11.038(2)	32.091(11)
β (deg)	96.08(3)	125.81(2)
V (Å^3)	3645.3(13)	7192(3)
Z	4	8
ρ_{calc} (g cm^{-3})	1.618	1.476
μ (mm^{-1})	4.334	4.316
F(000)	1776	3216
	Data Collection	
T (K)	140(2)	140(2)
scan mode	ω	ω
hkl range	$-34 \rightarrow +33, -17 \rightarrow +17, -14 \rightarrow +13$	$-28 \rightarrow +28, -13 \rightarrow +13, -38 \rightarrow +38$
measd reflns	31 409	66 176
unique reflns [R_{int}]	8755 [0.0985]	12 657 [0.0470]
reflns used for refinement	8755	12657
	Refinement	
refined param	451	817
GOF on F^2	1.003	1.004
R1,[a] wR2[b] all data	0.0437, 0.0791	0.0492, 0.1241
ρ_{fin} (max/min) (e Å^{-3})	1.258, −0.550	2.487, −1.624

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$.

are slightly longer than those found in $[\mathbf{II}\text{-}\mu_2\text{-F}]^-$ [2.589(2) Å], which possesses a less sterically hindered and possibly more Lewis acidic Hg center. Nevertheless, they remain within the range observed in other complexes such as $[(CF_3)_2Hg(\mu_2\text{-}F)_2Hg(CF_3)_2]^{2-}$ (2.39 and 2.42 Å)[27] or the fluoride adduct of a tetranuclear mercuracarborand (2.56 and 2.65 Å).[4] In comparison to $[\mathbf{II}\text{-}\mu_2\text{-F}]^-$, it is also interesting to note that the longer Hg−F distances observed in [**4**-μ_2-F] correlate, as expected, with a smaller $^1J_{Hg-F}$. Coordination of the fluoride results in substantial pyramidalization of the B centers [$\Sigma_{C-B1-C} = 338.5°$ (**A**) and 340.9° (**B**)] along with an increased deviation of the C−Hg−C angles [162.2(2)° (**A**) and 164.1(2)° (**B**)] from linearity. This deviation is comparable to that observed in the anionic complex $[(CF_3)_2Hg(\mu_2\text{-}F)_2Hg(CF_3)_2]^{2-}$ [162.1(5)°][27] and provides further

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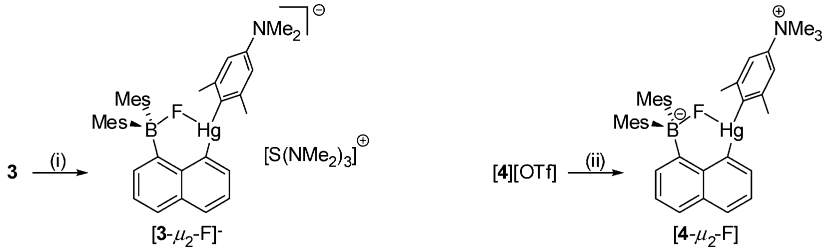
Scheme 2[a]



[a] (i) [Me_3SiF_2][$S(NMe_2)_3$], CH_2Cl_2, 25 °C, 71%. (ii) [Me_3SiF_2][$S(NMe_2)_3$], CH_2Cl_2, 25 °C, 62%.

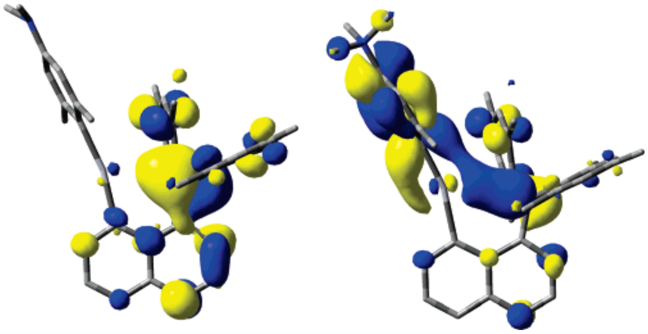


Figure 2. Optimized geometries and LUMOs (isodensity value = 0.03) of **3** (left) and [**4**]$^+$ (right).

Table 2. NMR Spectroscopy Data for [**II**-μ_2-F]$^-$,[13] [**3**-μ_2-F]$^-$, and [**4**-μ_2-F]

	[**II**-μ_2-F]$^-$	[**3**-μ_2-F]$^-$	[**4**-μ_2-F]
δ(^{11}B) in ppm	8.5	8.7	8.9
δ(^{19}F) in ppm	−164.3	−165.1	−164.7
δ(^{199}Hg) in ppm	−811.8	−708.6	−759.8
$^1J_{Hg-F}$ in Hz	135.2	109.8	122.0

evidence for the presence of a significant interaction between the Hg and F atoms in [**4**-μ_2-F].

Calculations. The structures of **3** and [**4**]$^+$ have been optimized using DFT methods. The two structures are very similar and show separations of 3.38 Å (**3**) and 3.32 Å ([**4**]$^+$) between the B and Hg atoms. This distance is comparable to the separation of 3.328(4) Å observed in the crystal structure of [**4**][OTf]. The secondary Hg−π interaction involving the *ipso*-C atom of one of the mesityl groups and the Hg atom is also present in the optimized structure of [**4**]$^+$ (3.04 Å) and can be compared to the distance of 3.022(4) Å observed in the crystal structure of [**4**]$^+$. As shown in Figure 2, the lowest unoccupied molecular orbital (LUMO) of **3** is dominated by the B atom. By contrast, the LUMO of [**4**]$^+$ is distributed between the two Lewis acidic elements and features a lobe that spans the B and Hg centers. This orbital also shows a substantial contribution from an antibonding E orbital of the benzene core of the aniline moiety. The difference observed in the makeup of the LUMO of these two molecules indicates that conversion of the amino group into an ammonium group on going from **3** to [**4**]$^+$ results in a lowering of the Hg vacant orbitals, allowing them to mix more efficiently with the B orbital. In turn, it can be anticipated that the Hg center of [**4**]$^+$ will show an increased participation in the binding of anionic guests.

F$^-$ Anion Binding Studies. In order to determine how the anion binding properties of such receptors are influenced by the presence of a cationic ammonium group, the fluoride binding properties of **3** and [**4**]$^+$ have been studied and compared. The addition of TBAF to a THF solution of **3** and [**4**]$^+$ results in a decrease of the absorbance at 363 and 362 nm for **3** and [**4**]$^+$, respectively. This phenomenon results from population of the empty B p orbital, which can no longer promote conjugation throughout the molecule. Examination of the binding isotherm obtained for both **3** and [**4**]$^+$ shows a linear decrease of the absorbance, which reaches the baseline after the addition of exactly 1 equiv. These results indicate the formation of the 1:1 complexes [**3**-μ_2-F]$^-$ and [**4**-μ_2-F], whose stability constants exceed the value of 10^7 M^{-1} measurable by a UV−vis titration. Bearing in mind that the stability constant of [Mes_3BF]$^-$ is equal to 3.3 (±0.4) × 10^5 M^{-1} in THF,[9] these results suggest that the fluoride ion affinity of **3** and [**4**]$^+$ is increased mainly by a chelate effect. Both **3** and [**4**]$^+$ also complex fluoride in THF/water (9/1, v/v) mixtures. In this more competitive medium, the fluoride binding constants of **3** and [**4**]$^+$ are clearly differentiated and are respectively equal to 1.3 (±0.1) × 10^2 and 6.2 (±0.2) × 10^4 M^{-1} (Figure 3, top). The enhanced fluoride binding constant of [**4**]$^+$ when compared to **3** confirms that the chelate effect occurring in these types of fluoride receptors can be combined with favorable Coulombic attractions to strengthen the host−guest interaction. We also note that, despite its cationic character, [**4**]$^+$ remains highly selective for fluoride over other environmentally abundant anions. For example, the addition of 10 equiv of Cl$^-$, Br$^-$, NO_3^-, $H_2PO_4^-$, and HSO_4^- does not significantly affect the UV−vis spectrum of a 4.5 × 10^{-5} M solution of [**4**]$^+$ in THF/H_2O (9/1, v/v), while the same experiment carried out with F$^-$ leads to a 93% decrease of the absorbance at 363 nm (Figure 4). A weak response is detected with OAc$^-$ (9% absorbance decrease upon the addition of 10 equiv), which is usual for B-based Lewis acids.[8] Because of the spontaneous formation of I_3^- under these conditions, UV−vis spectroscopy could not be used to study iodide binding. However, NMR studies in DMSO-*d*$_6$ show that iodide does not interact with [**4**]$^+$. Finally, the addition of an aqueous solution of Al^{3+} to a solution containing [**4**-μ_2-F] leads to complete regeneration of [**4**]$^+$, showing that fluoride binding is reversible (Figure 3, bottom).[15]

Conclusion

The results reported in this paper show that the fluoride binding constant of heteronuclear B/Hg bidentate Lewis acids can be substantially increased by introduction of a cationic

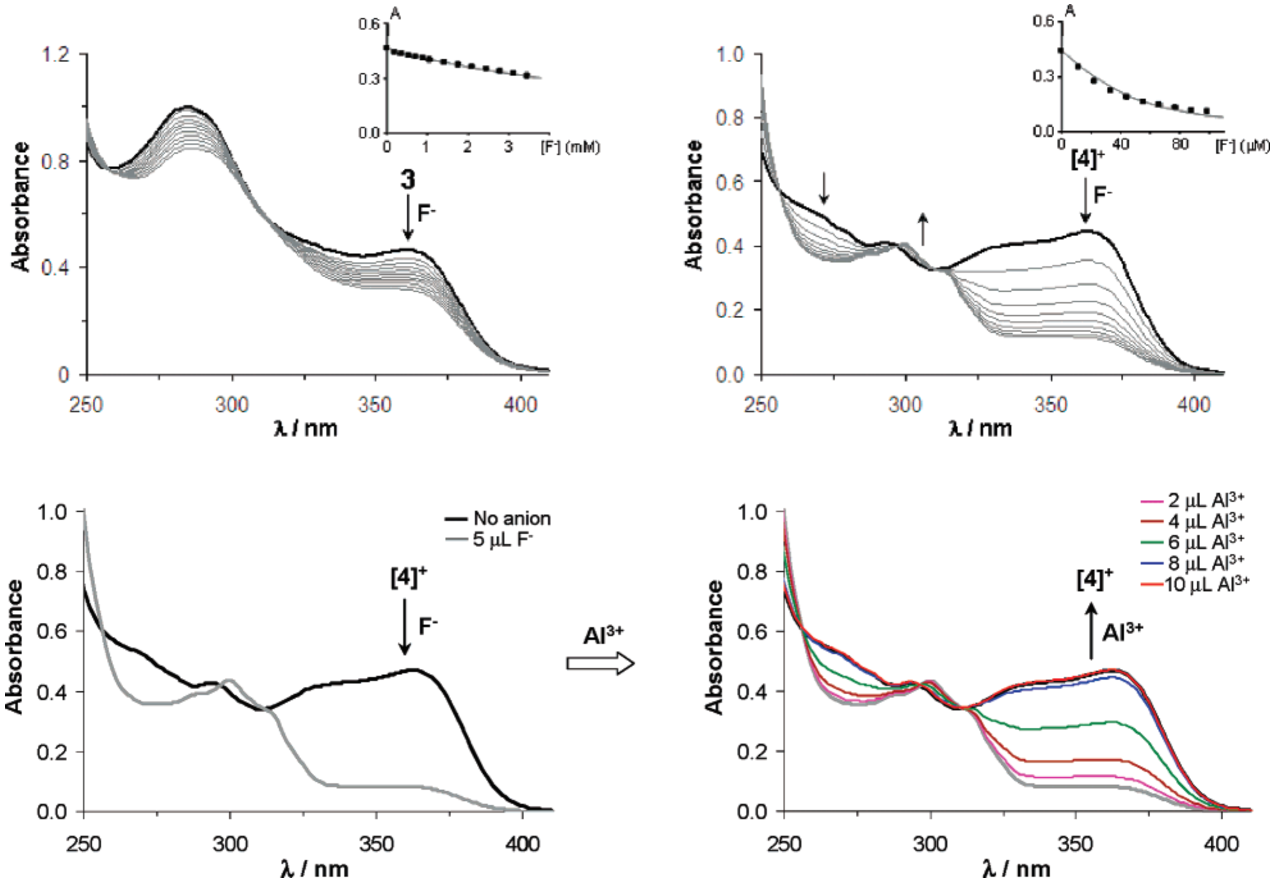


Figure 3. Top: Changes in the UV−vis absorption spectra of a solution of **3** and [**4**][OTf] [3 mL, 4.5 × 10^{-5} M in THF/H_2O (9/1, v/v)] upon the addition of a TBAF solution in THF. Bottom: Changes in the UV−vis absorption of a solution of [**4**][OTf] (3 mL, 4.5 × 10^{-5} M) in THF/H_2O (9/1, v/v) after the addition of a TBAF solution (left, 6.75 × 10^{-2} M in THF), followed by successive additions of an aqueous $AlCl_3$ solution (right, 0.01 M).

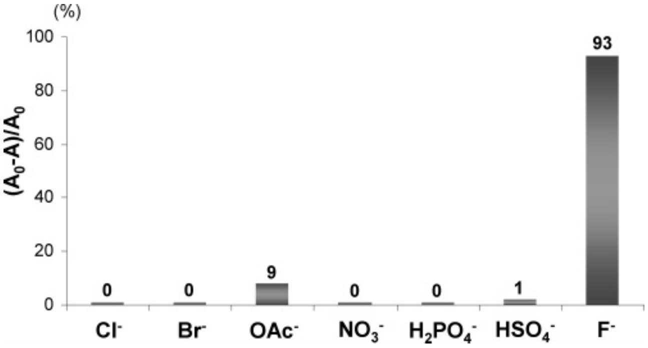


Figure 4. Percent decrease of the absorbance of a solution of [**4**][OTf] (4.5 × 10^{-5} M) in THF/H_2O (9/1, v/v) at 363 nm in the presence of 10 equiv of various anions.

moiety. This increase results from favorable Coulombic attractions that strengthen the host−guest interaction and ultimately complement the chelate effect occurring in these types of bidentate receptors. This study constitutes a useful milestone for the design of water-compatible fluoride sensors. Future improvement may require that the cationic moiety be directly attached to the triarylboron part of the receptor.

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Supporting Information Available: Optimized geometries of **3** and [**4**]$^+$, UV−vis titration data in THF, and X-ray crystallographic data for [**4**][OTf] and [**4**-μ_2-F] in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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