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A Heteronuclear Bidentate Lewis Acid as a Phosphorescent Fluoride Sensor

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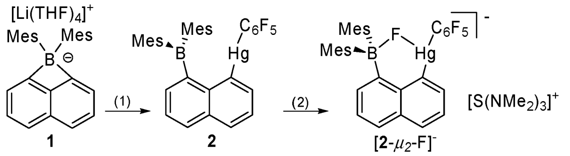
Fluoride displays a high hydration enthalpy ($\Delta H° = -504$ kJ/mol), and its molecular recognition in protic media is a definite challenge.[1] Several fluoride receptors that contain H-bond donors as binding sites have been investigated and used in nonprotic media.[1,2] However, as recently noted by Fabbrizzi,[2] such receptors typically cannot be used in the presence water that effectively competes with the receptor for the anion. For this reason, an impetus exists for the development of alternative strategies. One such strategy involves the use of bidentate Lewis acidic receptors that chelate the anion.[3,4] As part of our contribution to this general area, we recently demonstrated that appropriately substituted 1,8-diborylnaphthalenes[5,6] can be used as colorimetric fluoride sensors with binding constants that exceeds those of simple triarylboranes by at least 3 orders of magnitude.[7] In an extension of this chemistry, we would now like to describe the synthesis and properties of a heteronuclear bidentate Lewis acid which serves as a phosphorescent fluoride sensor.

As demonstrated by a recent report, multidentate mercury Lewis acids are competent for fluoride binding.[8,9] Keeping in mind that mercury can also serve to induce the room temperature phosphorescence of hydrocarbon chromophores[10] via spin−orbit coupling,[11] we decided to investigate the synthesis of a heteronuclear B/Hg bidentate Lewis acid whose phosphorescent properties could serve to signal fluoride complexation.

The $[Li(THF)_4]^+$ salt of dimesityl-1,8-naphthalenediylborate (**1**)[12] was allowed to react with C_6F_5HgCl to afford **2** as a pale yellow air- and water-stable derivative (Scheme 1). This compound, which is not soluble in water, has been fully characterized. Some of its salient spectroscopic features include (i) a ^{199}Hg NMR signal centered at −741.9 ppm and split into a triplet of triplets ($^3J_{Hg-F} = 499$ Hz and $^4J_{Hg-F} = 165$ Hz), and (ii) a ^{11}B NMR signal at 72 ppm. In the crystal (Figure 1), the boron atom B(1) adopts a trigonal planar geometry ($\Sigma_{(C-B-C)} = 359.9°$) and is separated from the mercury atom Hg(1) by only 3.300(9) Å. Owing to steric crowding, the mercury atom Hg(1) and boron atom B(1) are displaced by 0.40 Å on either side of the naphthalene plane. The short C(21)−Hg(1) distance of 3.000(7) Å indicates the presence of a secondary Hg−π interaction involving the *ipso*-carbon of one of the mesityl groups.[10] As a result, the C(8)−Hg(1)−C(31) (172.8(3)°) angles slightly deviate from linearity. As in other triarylboranes,[7] it can be expected that the unsaturated boron atom of **2** mediates conjugation of the naphthalenediyl and mesityl substituents, which collectively behave as a single chromophore. This is confirmed by the UV−vis spectrum of **2**, which features a broad absorption band at 361 nm ($\epsilon_{361} = 10\,200$ in THF) notably red-shifted when compared to the absorption of naphthalene ($\lambda_{max} = 286$ nm). Because of the spin−orbital perturbation provided by the mercury atom, photoexcitation of **2** in the solid state gives rise to an emission at $\lambda_{max} = 531$ nm, which most likely corresponds to the phosphorescence of the dimesitylborylnaphthalenediyl chromophore (Figures 2 and 3). The large Stokes shift of approximately 7100 cm^{-1} corroborates this assignment.

Scheme 1 ^{a}



^{a} (1) C_6F_5HgCl, THF, 25°C, 72%. (2) $[Me_3SiF_2]^-[S(NMe_2)_3]^+$, $CHCl_3$, 25 °C, 89%.

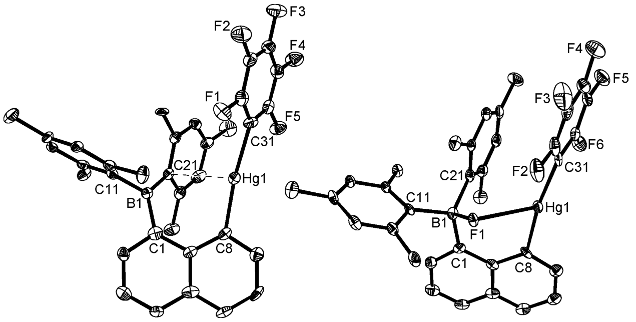


Figure 1. Crystal structure of **2** (left) and of the anionic component of $[\mathbf{2}\text{-}\mu_2\text{-F}]^-[S(NMe_2)_3]^+$ (right) (50% ellipsoid). Pertinent parameters are provided in the text.

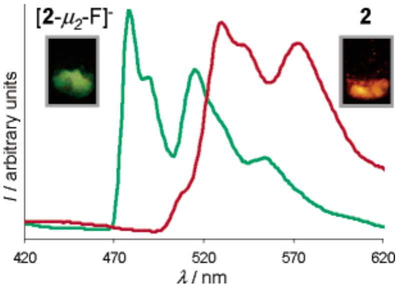


Figure 2. Solid state phosphorescence spectra of compounds **2** (red line) and $[\mathbf{2}\text{-}\mu_2\text{-F}]^-[S(NMe_2)_3]^+$ (green line) after excitation at 324 nm at 77 K. The pictures show the color of the emission observed under a hand-held UV lamp at 77 K.

Compound **2** readily chelates fluoride anions in a variety of solvents. For example, treatment of **2** with $[Me_3SiF_2]^-[S(NMe_2)_3]^+$ in chloroform leads to formation of $[\mathbf{2}\text{-}\mu_2\text{-F}]^-[S(NMe_2)_3]^+$ (Scheme 1). The ^{11}B NMR signal of $[\mathbf{2}\text{-}\mu_2\text{-F}]^-$ appears at 8.5 ppm, as expected for a tetrahedral boron atom. The ^{19}F NMR spectrum features a broad signal at −164.3 ppm, which is comparable to the chemical shift observed in other fluoride-bridged boron species.[4,5] Accordingly, the ^{199}Hg nucleus is coupled to the bridging fluoride ($^1J_{Hg-F} = 135.2$ Hz) and gives rise to a signal at −811.8 ppm split into a triplet of doublets of triplets ($^3J_{Hg-F} = 387.1$ Hz, and $^4J_{Hg-F} = 65.8$ Hz). Colorless crystals of $[\mathbf{2}\text{-}\mu_2\text{-F}]^-[S(NMe_2)_3]^+$ were obtained by slow evaporation of a $CHCl_3$ solution. As indicated by the X-ray crystal structure (Figure 1), the fluorine atom is bound to both Lewis acidic centers. The B(1)−F(1) bond length of 1.483(4) Å is not significantly longer than those found in triarylfluo-

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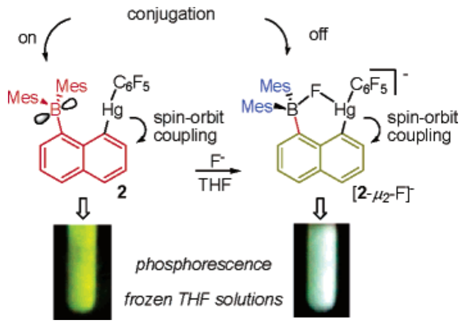

Figure 3. Figure depicting the effect of fluoride binding on the photophysical properties of **2**/[**2**-μ_2-F]$^-$. Luminescence detected for **2** and [**2**-μ_2-F]$^-$ in frozen THF solution.

roborate anions (1.47 Å),[7c] thus indicating the presence of a usual polar covalent B−F linkage. Because the accepting 6p orbitals of mercury might be too high to efficiently mix with the fluoride donor orbitals, the Hg(1)−F(1) bond of 2.589(2) Å is probably more electrostatic than covalent. Nevertheless, the length of this bond is within the sum of the van der Waals radii of the two elements[13,14] and is, in fact, comparable to those observed in a fluoride adduct of a tetranuclear mercuracarborand (2.56 and 2.65 Å).[8] In agreement with the above bonding description, the sum of the coordination angles at boron ($\Sigma_{(C-B1-C)} = 340.4°$) indicates substantial pyramidalization while the C(8)−Hg(1)−C(31) angle (170.8(2)°) only slightly deviates from linearity.

Since fluoride complexation leads to population of the boron-empty p-orbital, conjugation of the naphthalenediyl and mesityl substituents is no longer operative. As a result, the absorption band observed for **2** at 361 nm progressively disappears upon incremental addition of fluoride. When this experiment is carried out in THF, the absorbance at 361 nm linearly decreases and reaches the baseline after the addition of exactly 1 equiv. These results indicate the formation of a 1:1 complex whose stability constant exceeds the range measurable by direct titration ($K > 10^8$ M^{-1}). This stability constant exceeds that of [Mes$_3$BF]$^-$ in THF (3.3(0.4) × 10^5 M^{-1}) by at least 3 orders of magnitude.[5] When the same experiment was repeated in a 90:10 (v/v) THF/water mixture, fitting of the data on the basis of a 1:1 binding isotherm yields a stability constant of 2.3(±0.2) × 10^4 M^{-1}. This value is much larger than that measured for Mes$_3$B (1.0(±0.3) × M^{-1}) in the same THF/water mixture, which substantiates the cooperative binding of the fluoride by the boron and mercury atoms. Fluoride binding is remarkably selective since no changes are observed in the presence of chloride, bromide, iodide, cyanide, acetate, nitrate, sulfate, and phosphate. The charge neutrality of **2** combined with a sterically crowded binding pocket certainly contributes to the observed selectivity.

In the solid state, the energy and vibronic progressions observed in the emission spectrum of [**2**-μ_2-F]$^-$[S(NMe$_2$)$_3$]$^+$ correspond very closely to those observed in the phosphorescence spectrum of naphthalene (Figure 2).[10] This indicates that the loss of conjugation, triggered by fluoride binding at boron, leads to electronic isolation of the naphthalenediyl chromophore which readily phosphoresces (Figure 3). These results also indicate that the spin−orbital perturbation induced by the mercury atom is, a priori, not affected by fluoride binding. Most significantly, fluoride binding to **2** leads to the appearance of a new intense signal at 480 nm, where pure **2** does not emit. Under a hand-held UV lamp, solid **2** gives rise to a red emission which becomes pale green for [**2**-μ_2-F]$^-$ (Figure 2). A similar phenomenon is readily observed in frozen solutions. Thus, while a 2 × 10^{-3} M frozen THF solution of **2** gives rise to a yellow luminescence attributed to phosphorescence of the dimesitylboryl-naphthalenediyl chromophore, a white emission with a blue−green tint is readily observed for [**2**-μ_2-F]$^-$ when frozen in THF at the same concentration. These emissions, which only necessitate the use of a hand-held UV lamp as an excitation source, are extremely bright and can be readily detected with the naked eye (Figure 3). Addition of up to 2−3% of water does not affect the efficacy of the assay.

In conclusion, we report the synthesis of a heteronuclear bidentate Lewis acid which serves as a highly selective and sensitive phosphorescent fluoride sensor. The proximity of the two Lewis acidic sites enforced by the 1,8-naphthalenediyl backbone promotes fluoride anion chelation and is responsible for the high binding constant. The interplay of conjugative and spin−orbit coupling effects mediated by the boron and mercury atoms, respectively, results in the phosphorescent signaling of fluoride binding. To our knowledge, **2** is the first example of a *phosphorescent* anion sensor. Its ability to complex fluoride in partially aqueous media is also noteworthy, yet not unprecedented.[3a]

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Supporting Information Available: Experimental details and X-ray crystallographic data for **2** and [**2**-μ_2-F]$^-$[S(NMe$_2$)$_3$]$^+$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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