



Note

Multi-step detection of cyanide ion by a bis(dimesitylboryl)dibenzoazaborine

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ABSTRACT

A bis(dimesitylboryl)dibenzoazaborine formed Lewis acid–base type complexes with up to two cyanide ions in stepwise fashion. The complex formation constants for cyanide ion were larger than those for fluoride ion, despite the higher affinity of fluoride ion to boron atoms than that of cyanide ion.

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1. Introduction

High-performance of capture and detection of biologically and environmentally active ions is currently one of the most important subjects in the field of host–guest and analytical chemistry. Among many anions, cyanide ion has a prominent position, due to its high toxicity and industrial importance, and thus the development of efficient ion sensors against it is desired [1,2]. In order to develop optical anion sensor, triarylborane is an attractive building unit of choice, because of its strong Lewis acidity as well as the switching ability of electronic and optical properties upon the complexation [3]. Such characteristics have prompted recent advance in triarylborane-based cyanide ion sensors [4].

Recently, we have reported the synthesis and properties of dibenzoheteraborins, hetero- π -conjugated molecules containing a main group element and a boron atom as an electron donor and acceptor, respectively, and their π -extended derivatives [5]. The optical properties of dibenzoheteraborins as well as the Lewis acidity of the boron atoms could be controlled by the main group elements incorporated, and efficient fluoride or cyanide ion detection using dibenzoazaborines or dibenzophosphaborins was accomplished [6]. In this course, we synthesized bis(dimesitylboryl)dibenzoazaborine **1** as an azaborine bearing a strong electron acceptor and found that this molecule works as two-step fluoride ion sensor (Scheme 1, A = F) [7]. Although other dibenzoheteraborins lose their fluorescence emission ability upon the fluoride complexation, fluoride complexes **2a** and **2b** exhibited still strong but differently colored fluorescence. This property is quite useful for

fluorescence detection of anions (especially anion sensing with naked eyes) compared with ordinary “ON–OFF” type fluorescence sensor. Herein, we wish to report the application of **1** to fluorometric sensing of cyanide ion.

2. Results and discussion

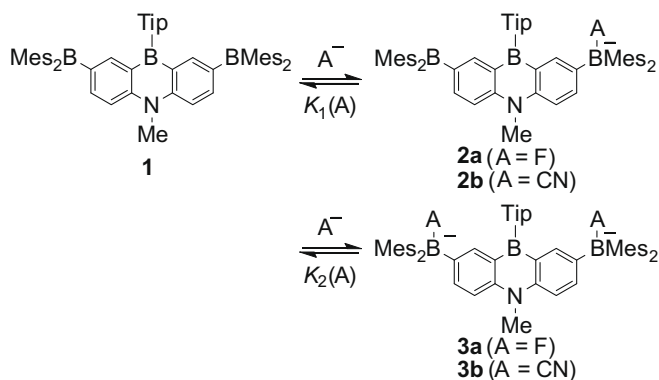
First, we tried the reaction between an inorganic cyanide ion source with **1**. The reaction between **1** and solid NaCN in THF- d_8 was monitored by ^{11}B NMR spectroscopy, and the spectral change is depicted in Fig. 1. Before the mixing of NaCN, **1** exhibited a broad signal around δ_{B} 65, which is assigned to the overlapped signals of the dimesitylboryl groups and the central boron atom. Two hours after the mixing, a new signal developed at δ_{B} –15 that is attributable to the resonance of a cyanoborate, judging from the reported chemical shifts of triaryl cyanoborates [6a]. The intensity of this signal increased slowly, and after two days, the spectral change was converged.

This reaction was also monitored by UV–Vis spectroscopy. Because the reaction was very slow, probably owing to the low solubility of NaCN in THF, the completion of the reaction needed two days (Fig. 2). Comparing the spectral band shape with that of the reaction of **1** with fluoride ion [7], the generated cyanoborate may be **2b**, i.e. the complexation occurred at the dimesitylboryl groups. However, the precise information about this reaction, such as complexation constants, could not be obtained, because the reaction was carried out in a biphasic condition between the solution and the solid states. Therefore, we next tried to the cyanide ion complexation by using $(n\text{-Bu})_4\text{NCN}$ as a soluble cyanide ion source.

A dilute solution of **1** ($[\mathbf{1}] = 1.1 \times 10^{-5} \text{ M}$) in THF was titrated with a THF solution of $(n\text{-Bu})_4\text{NCN}$ by using UV–Vis and fluores-

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Scheme 1. Two-step anion complexation by **1**. A = F or CN. $K_1(\text{A})$ and $K_2(\text{A})$ denote complex formation constants of **1** against these anions.

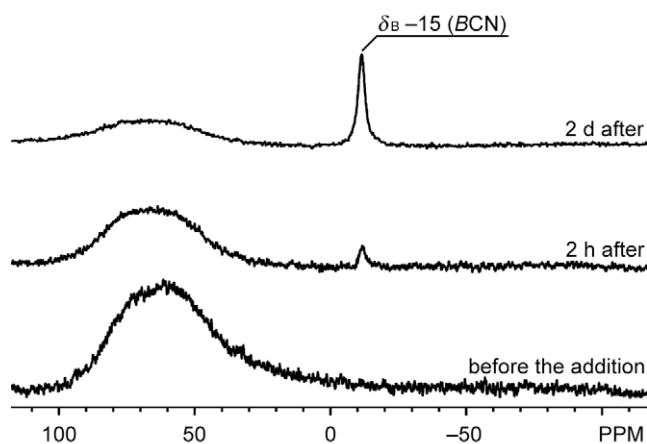


Fig. 1. ^{11}B NMR spectra of the reaction mixture containing **1** and solid NaCN in THF- d_8 at rt.

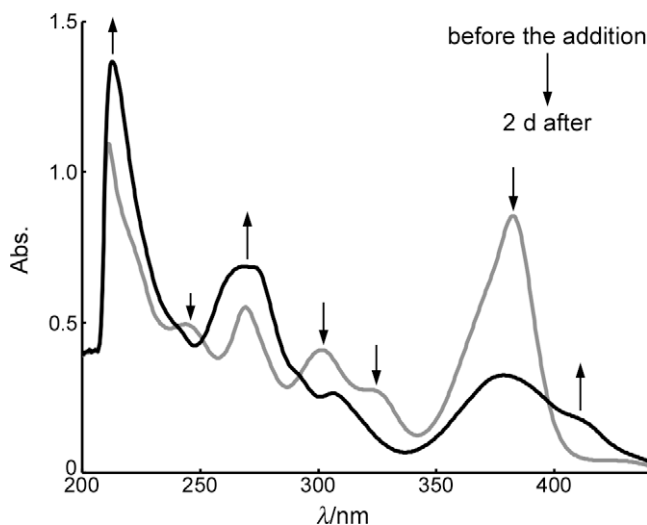


Fig. 2. UV-Vis spectral change of **1** upon addition of excess solid NaCN in THF at rt ($[\text{1}] = 1.2 \times 10^{-5} \text{ M}$).

cence spectroscopy (Fig. 3). Two distinct reactions occurred in stepwise fashion. Until the addition of 1 equiv. of cyanide ion, the absorption bands changed with a set of isosbestic points, indicating the formation of single product. In addition, the spectral

change is similar to that observed in the complexation of fluoride ion by **1**. By analogy with the molecular structure of fluoroborate **2a**, the generated cyanoborate was assigned to **2b**. Further addition of cyanide ion resulted in the appearance of a new set of isosbestic points, and the spectral change was finished by the addition of 3 equiv. of cyanide ion. Again, from the comparison of the spectral shape with that observed in the fluoride complexation reaction, the product in this step was deduced to be biscyanoborate **3b**. The longest absorption maximum was shifted to 420 nm, which is between the absorption maximum of a parent dibenzoazaborine and those of dibenzoazaborines bearing amino groups, strong electron-donors [5]. This also confirms that the molecular structure of the biscyanoborate is **3b** that has a dibenzoazaborine core with electron-donating cyanoborate moieties. Such stepwise complexation indicates that the value of $K_1(\text{CN})$ is much larger than that of $K_2(\text{CN})$ in Scheme 1. If not, the addition of cyanide ion results in the formation of a mixture of **1**, **2b**, and **3b** and the isosbestic points can not be observed.

This reaction could be also monitored by fluorescence spectroscopy. Under UV irradiation (λ_{ex} 295 nm), the addition of cyanide ion into the THF solution of **1** resulted in the red-shift of the emission maximum, and finally a strong emission (λ_{em} 433 nm) was observed after the addition of 2.6 equiv. of cyanide ion. The fluorescent-color change from violet to blue could be seen with naked eyes. Therefore, **1** can be utilized as a fluorescent-color change type sensor, in sharp contrast to ordinary triarylborane-based “ON-OFF” type anion sensors including the previous heteroazaborines-based anion sensors.

In order to evaluate the anion-recognition performance of **1**, the complex formation constants were estimated by using a non-linear least-square fitting analysis of the UV-Vis titration data [8]. The experimental data points as well as the estimated fitting curves are shown in Fig. 4. However, the complexation ability of **1** against cyanide ion was too high to estimate exact formation constants, and thus only orders of the constants are shown here (Table 1). We have also tried to solve the problem by using the Benesi-Hildebrand plot as well as a numerical fitting assuming the stepwise complexation, but these methods were unsuccessful. Although both the values of $K_1(\text{CN})$ and $K_2(\text{CN})$ exceed the limit of precise estimation ($>10^8 \text{ M}^{-1}$), the former should be much larger than the latter (*vide supra*). Compared with the complexation with fluoride ion, **1** seems to form much stronger complexes with cyanide ion in a THF solution. Although fluoride ion can strongly coordinate to a boron atom due to its large Lewis basicity and hardness, concomitant water in commercial ($n\text{-Bu}$) $_4\text{NF}$ may depress its reactivity. Water molecules are known to strongly coordinate fluoride ion and hamper the complexation with Lewis acids [9].

The origin of the enhanced complexation ability of **1** against fluoride or cyanide ion is intriguing. The electronic interaction between the two dimethylboryl groups through the dibenzoazaborine skeleton is assumed to lower the LUMO energy level and increase the Lewis acidity compared to an ordinary triarylborane with a similar steric congestion around the boron center, such as PhBMe_2 . In order to verify this notion, DFT calculations on **1'**, monoboryldibenzoazaborine **4**, di-benboazaborine **5**, and PhBH_2 (**6**) were performed (Fig. 5). The calculations were carried out by using GAUSSIAN 03 program package [10], and B3LYP/6-31G+(d) level of theory was employed for geometry optimizations and single point energy calculations.

The calculated energies of the frontier orbitals of **1'**, **4**, **5**, and **6** are listed in Table 2. Parent dibenzoazaborine **5** has the highest HOMO and LUMO among the compounds. The introduction of a BH_2 group into the dibenzoazaborine skeleton decreases the energy level of frontier orbitals by *ca.* 0.3 eV. The LUMO energy of **4** is -2.03 eV , which is comparable to that of **6**, indicating that these two boranes will exhibit similar Lewis acidity and complexation

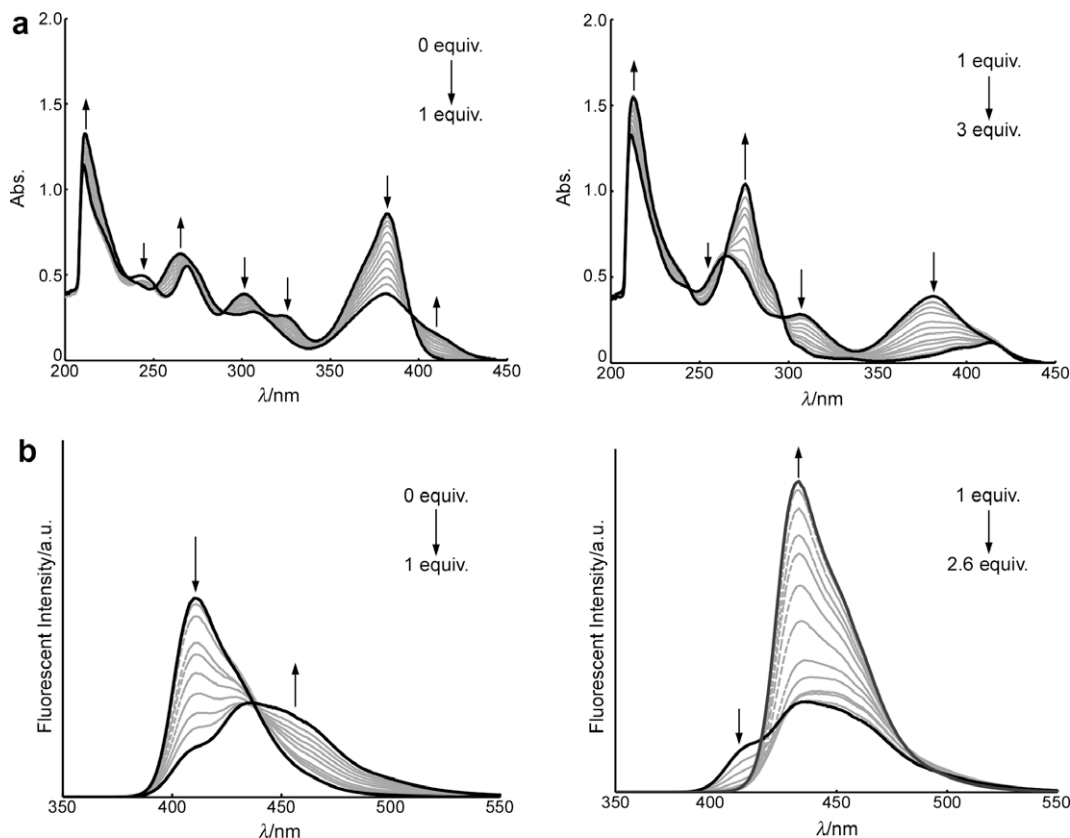


Fig. 3. UV-Vis (a) and fluorescence (b) spectral change of **1** upon addition of (n-Bu)₄NCN in THF at rt ([**1**] = 1.0 × 10⁻⁵ M).

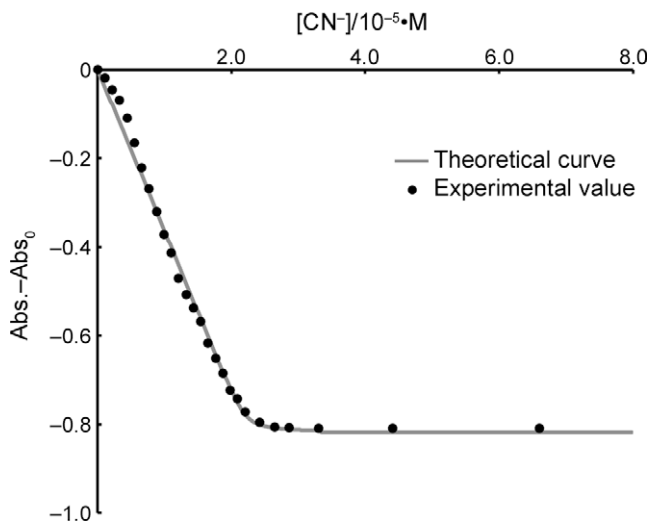


Fig. 4. The fitting curve for the cyanide complexation reaction.

Table 1

The complex formation constants between **1** and anions.

	$K_1(A)$ (M ⁻¹)	$K_2(A)$ (M ⁻¹)
Cyanide	>10 ⁸	>10 ⁸
Fluoride ^a	>10 ⁸	7(1) × 10 ⁵

^a In Ref. [7].

behavior against Lewis bases. Owing to the additional effect of another BH₂ groups, the LUMO of bisboryl derivative **1'** is located at

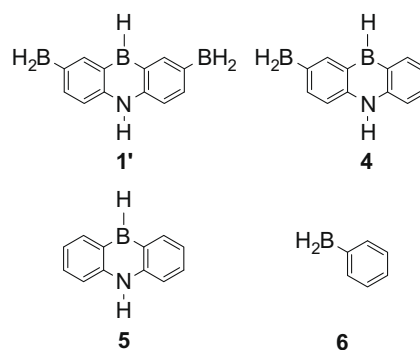


Fig. 5. Model compounds used in the theoretical calculations.

Table 2

Frontier orbital energies of **1'**, **4**, **5**, and **6**.

	HOMO (eV)	LUMO (eV)
1'	-6.40	-2.34
4	-6.10	-2.03
5	-5.77	-1.73
6	-7.26	-2.15

the lowest energy level among these compounds. Therefore, **1'** is thought to be the stronger Lewis acid compared to the ordinary monoborane compounds, like **6**. Such synergistic effect of the two boron groups may be the main reason for the enhanced Lewis acidity of **1**. In addition, the anionic charge of monocyanoborate **2b** can be stabilized by the electron-withdrawing property of another Mes₂B group, and this effect also enhances the Lewis acidity of **1**.

In conclusion, cyanide ion recognition by a bis(dimesitylboryl)dibenzoazaborine was investigated with UV–Vis and fluorescence spectroscopy. As same as the case of complexation of the same azaborine with fluoride ion, the azaborine reacted with cyanide ion in two-step fashion to give mono- and biscyanoborates, and this reaction could be monitored by fluorescent-color change. Compared with the fluoride complexation, the cyanide formed complexes with larger complexation constants, probably because of the retarded Lewis basicity of fluoride ion due to concomitant water. The enhanced Lewis acidity of the bis(dimesitylboryl)azaborine is owing to the synergetic interaction of the two boryl groups.

3. Experimental

3.1. General

General chemicals were used as received. For optical measurements, commercial spectrochemical or fluorometric grade solvents were used. NMR spectra were recorded on a JEOL AL-400 spectrometer. UV–Vis spectra and fluorescence spectra were measured with a JASCO V-670 spectrophotometer and a JASCO FP-6500 fluorescence spectrophotometer, respectively. The synthesis of **1** has been described previously [7].

3.2. NMR monitoring of the reaction of **1** with NaCN

In a 5 mm ϕ NMR tube, to a THF- d_8 (0.5 mL) solution of **1** (23 mg, 0.026 mmol) was added powdered NaCN (20 mg, 0.41 mmol), and the reaction was monitored by ^{11}B NMR spectroscopy at rt.

3.3. UV–Vis monitoring of the reaction of **1** with NaCN

In a capped quartz cell, to a solution of **1** (1.2×10^{-5} M solution in THF, 3.0 mL, 3.6×10^{-8} mmol) was added powdered NaCN (20 mg, 0.41 mmol), and the reaction was monitored by UV–Vis spectroscopy at rt.

3.4. UV–Vis and fluorescence monitoring of the reaction of **1** with (*n*-Bu) $_4$ NCN

In a capped quartz cell, to a solution of **1** (1.1×10^{-5} M in THF, 3.0 mL, 3.3×10^{-8} mmol) was added (*n*-Bu) $_4$ NCN (3.3×10^{-3} M in THF), and the reaction was monitored by UV–Vis and fluorescence spectroscopy. From the absorption change at 383 nm, complex formation constants were estimated by using a non-linear least-square fitting program.

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