

Phosphate anion-selective recognition by boron complex having plural hydrogen bonding sites†

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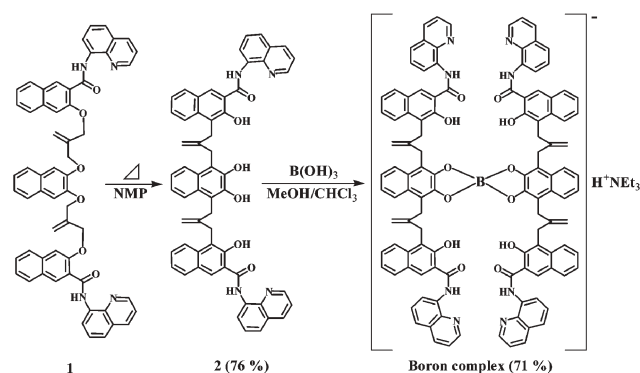
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A boron complex having plural proton donors (OH, amide NH) and proton acceptors (quinoline) acted as a selective chromo-ionophore toward phosphate anions in CH_3CN .

Self-assembly of polydentate ligands, having several coordination sites, assisted by metal ions is currently of interest in the field of supramolecular chemistry.¹ The highly organized supramolecular metal complexes often possess binding sites and cavities toward other cations,^{2,3} anions,^{2,4} and organic molecules.^{2,5} Recently, we have reported that the complexation of the catechol ligand bearing methyl naphthoate moieties with boric acid selectively gave a boron complex composed of ligand:boron = 2:1, and the boron complex was able to bind a lanthanoid ion by using the coordination ability of the methyl naphthoate moieties introduced into the end position in the ligand.⁶

In this work, we synthesized a novel boron complex appended not only with plural hydroxy and amide (NH) groups as proton donors but also with quinolines having both proton acceptor and optical response (chromophore) properties. Both the binding and the recognition abilities of the boron complex toward various anions in CH_3CN were studied by UV/VIS absorption spectrophotometry and $^1\text{H-NMR}$.

Scheme 1 shows the synthesis of the ligand and the boron complex. The novel catechol ligand **2** was obtained *via* tandem Claisen rearrangement of the corresponding polyether compound **1** (160 °C, 1 h, in *N*-methylpyrrolidinone).† Complexation between the ligand and the excess amount of $\text{B}(\text{OH})_3$, in the presence of



Scheme 1 Synthesis of novel boron complex.

† Electronic Supplementary Information (ESI) available: synthesis of polyether **1**, spectroscopic data of ligand **2** and its boron complex, NMR titration plot, and derivation of equation for determination of K_1 and K_2 . See <http://www.rsc.org/suppdata/cc/b4/b414901g/>

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triethylamine as base, in CHCl_3 -methanol was carried out under refluxing conditions. The solvent was removed by the evaporation, and then the residue was washed with the small amount of methanol and CHCl_3 . ESI-MS (anionic mode) of an acetonitrile solution of the obtained residue showed only one peak at m/z 1791, $[\text{2Ligand} + \text{B}^{3+} - 4\text{H}]^-$ corresponding to a mononuclear complex composed of Ligand:B = 2:1. The $^1\text{H NMR}$ spectrum of the boron complex in CDCl_3 gave the structural information in which the hydroxy groups of catechol moiety participated in the complexation with boron on the basis of the disappearance of those hydroxy protons. Furthermore, since there are half the number of peaks to protons for the ligand and a quarter per complex due to symmetry, the complex has the symmetrical four coordinated structure.† The boron complex not only has proton donating groups such as the hydroxy and the amide (NH) groups but also has proton accepting groups such as quinoline ring. Therefore, the boron complex is expected to bind and recognize anions although the boron complex has negative charge.

The binding and recognition abilities of the boron complex toward various anions in polar solvent such as CH_3CN were studied by using UV/VIS absorption spectrophotometry. The absorption spectra of the boron complex in the absence and presence of various anions having tetrabutylammonium ion as counter cation were measured in CH_3CN . The absorption spectrum of the boron complex was not varied by the addition of F^- , Cl^- , Br^- , I^- , CH_3COO^- , and HSO_4^- . On the other hand, when only H_2PO_4^- was added to the solution of the boron complex, the spectrum changed and two isosbestic points at

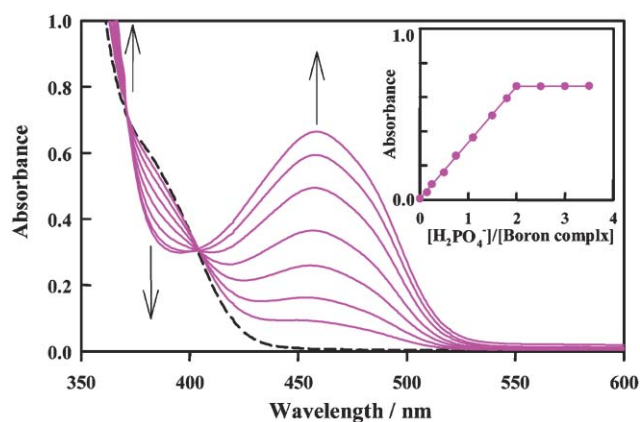


Fig. 1 Absorption spectra of the 2.1×10^{-5} M boron complex in the presence of $0-7.4 \times 10^{-5}$ M $[(\text{C}_4\text{H}_9)_4\text{N}]^+[\text{H}_2\text{PO}_4]^-$ in CH_3CN . Inset shows the molar ratio plot against the apparent absorbance at 460 nm.

371.5 nm and 403.5 nm were observed as shown in Fig. 1. This indicates the existence of two equilibria containing three components, *i.e.*, free boron complex and two boron complexes with one and two H_2PO_4^- anions captured respectively. The inset in Fig. 1 also shows the relationship between the variation of the absorption spectra at 460 nm and the molar ratio of H_2PO_4^- to the boron complex in the solution. The molar ratio plot obviously indicated an intersection at the molar ratio of 2, which corresponds to a 1:2 (= Boron complex: H_2PO_4^-) stoichiometry as expected from two isosbestic points.

$^1\text{H-NMR}$ study was performed to clarify the selective recognition of the boron complex toward H_2PO_4^- . Both peaks of the hydroxy protons and the amide (NH) protons in the boron complex were shifted to the lower magnetic field by the complexation with H_2PO_4^- .[†] This result exhibits the existence of hydrogen bonding between the hydroxy protons, the amide (NH) protons and H_2PO_4^- even in polar solvent such as CD_3CN . Similar spectral changes were also observed in the presence of F^- and CH_3COO^- having larger basicity (acid-dissociation constant: $\text{p}K_a$) than the other anions. For HSO_4^- , Cl^- , Br^- , and I^- , the chemical shifts of the hydroxy and amide NH protons were not changed, *i.e.*, the formation of a hydrogen-bonded complex between the boron complex and those anions had not occurred. Fig. 2 shows the variation of the chemical shift of the amide NH proton ($\Delta\delta_{\text{obs}} = \delta_{\text{app}} - \delta_{\text{Boron}}$) on the complexation of the boron complex with anions, where δ_{Boron} and δ_{app} express the chemical shift of the free boron complex and the apparent chemical shift of the boron complex in the presence of anions, respectively. The binding constant of the boron complex with anion was determined by using the general equation[†] derived with respect to $\Delta\delta_{\text{obs}}$ in Fig. 2. The largest K_1 and K_2 values for H_2PO_4^- can be rationalized on the basis of the basicity and that the structure consists of two oxygens and two acidic protons. When the boron complex makes hydrogen bonds with H_2PO_4^- , the nitrogen atom in the quinoline ring is expected to act as a proton acceptor and take part in the hydrogen-bond formation as shown in Fig. 3. Therefore, the boron complex can form more stable multitopic hydrogen bonding with H_2PO_4^- than F^- and CH_3COO^- which do not have acidic protons.

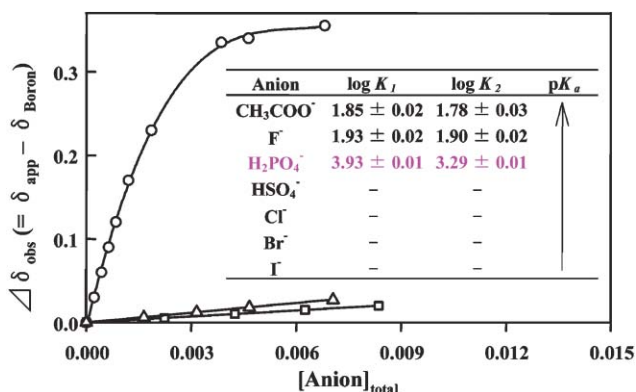


Fig. 2 Variation of the chemical shift of the amide NH proton in the boron complex in the presence of anions (\circ H_2PO_4^- ; \triangle F^- ; \square CH_3COO^-) in CD_3CN . Inset shows the binding constant of the boron complex with anions in CD_3CN at 25 °C. $K_1 = [\text{Boron-Anion}]/([\text{Boron}][\text{Anion}])$, $K_2 = [\text{Boron-2 Anion}]/([\text{Boron-Anion}][\text{Anion}])$.

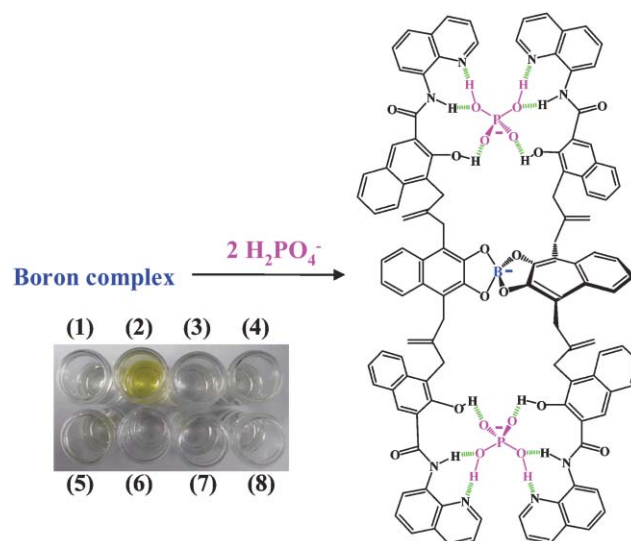


Fig. 3 Proposed complexation of the boron complex with H_2PO_4^- and color development of the 2.1×10^{-5} M boron complex in CH_3CN in the absence (1) and the presence of 4.2×10^{-3} M anion such as H_2PO_4^- (2), CH_3COO^- (3), HSO_4^- (4), F^- (5), Cl^- (6), Br^- (7), and I^- (8).

It was elucidated that the boron complex having plural proton donors (OH and amide NH) and proton acceptors (quinoline) is able to bind two H_2PO_4^- in CH_3CN (Fig. 3). The colorless solution of the boron complex became yellow after the boron complex selectively recognized H_2PO_4^- as can be seen by inspection of Fig. 1. This phenomenon is ascribed to the formation of hydrogen bonding between the nitrogen atom in quinoline as the optical response part and the acidic protons of H_2PO_4^- . For the F^- and CH_3COO^- cases, color (spectra) changes of those solutions did not occur because there was no hydrogen bonding between the nitrogen atom in quinoline and those anions although the boron complex could capture those anions by using the hydrogen bonding with the hydroxy and the amide protons as can be seen in NMR study.

Thus, we have successfully developed a novel chromionophore based on the boron complex exhibiting a selective recognition and coloration for H_2PO_4^- .

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