Synthesis of the Boron Complex Composed of the Noncyclic Ligands Having Plural Hydroxy Groups and the Binding Ability Toward Lanthanoid Ions

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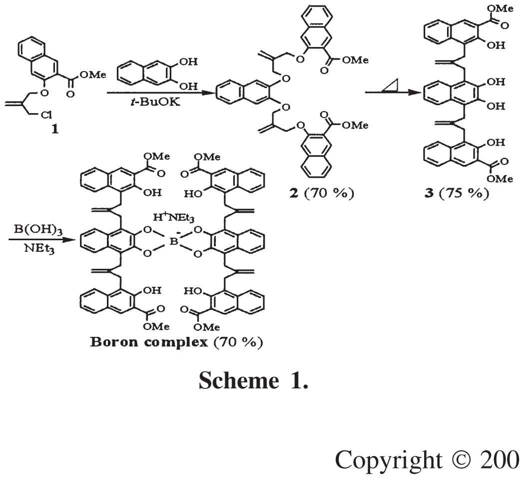
The boron complex composed of the noncyclic ligand having plural hydroxy groups behaves as a complex ligand and a forms hetero-binuclear complex with a lanthanoid ion.

Various ligands having several coordination sites such as hydroxy groups, amide, pyridine, pyrrole, and phenanthroline have been developed, and are currently of interest in the field of supramolecular chemistry.[1] Self-assembly of the noncyclic ligands assisted by metal ions and anions gave the higher ordered supramolecular structures such as helicates, cube, and cage compounds which can behave as host molecules having the ability of the molecular recognition.[2] For example, it has been reported that the noncyclic ligands and the noncyclic-macrocyclic complexes bearing some catechol units form supramolecular clusters with metal ions (e.g., B^{III}, Al^{III}, Fe^{III}, Zn^{II}, Ga^{III}, Ti^{IV}, Sn^{IV}, Mo^{VI}), and those clusters are able to recognize another metal ions and organic molecules.[3] On the other hand, we have reported that the isobutenyl bis(aryl ether) derivatives are easily converted into the compounds having two hydroxy groups via thermal reaction, so called "tandem Claisen rearrangement."[4] By using this tandem Claisen rearrangement, various ligands having plural hydroxy groups which possess the complexation ability toward transition metal ions and anions such as fluoride have been designed till now.[5]

In the present work, we synthesized a novel noncyclic ligand having plural hydroxy groups via tandem Claisen rearrangement. Complexation of the ligand with boric acid was carried out, moreover, and the binding ability of the obtained boron complex toward lanthanoid ions was investigated by using the electronic absorption spectroscopy.

The synthesis of the ligand is shown in Scheme 1. The reaction between 2-hydroxy-3-naphthoic acid methyl ester and the excess amount of 3-chloro-2-chloromethyl-1-propene in the presence of *t*-BuOK in DMF mainly gave compound **1**. The polyether compound **2** was prepared from compound **1** and 2,3-dihydroxynaphthalene in DMF under Ar atmosphere. The thermal reaction (tandem Claisen rearrangement) of the polyether compound **2** in decalin at 160 °C for 3 h afforded the ligand **3** having four phenolic hydroxy groups in good yield.[6]



Scheme 1.

Complexation of the ligand **3** (L) with boric acid was carried out. The reaction of L with 0.5–5 equiv. of $B(OH)_3$ in the presence of triethylamine as base in methanol at room temperature (or refluxing condition) resulted in pale yellow solid (Scheme 1). ESIMS (anion mode) of an acetonitrile solution of the solid showed a peak at m/z 1343, $[2L + B^{3+} - 4H]^-$ corresponding to a mononuclear complex composed of L:B = 2:1. ^1H NMR spectrum of the mononuclear complex in $CDCl_3$ gave the structure information in which the phenolic hydroxy groups of catechol moiety take part in the complexation with boron on the basis of the disappearance of those hydroxy protons, and the complex has the symmetrical four coordinated structure because each protons of two ligands have same chemical shifts.[7] The boron complex not only has a negative charge but also has the hydroxy groups and the carbonyl groups of ester moiety as shown in Scheme 1, therefore, the boron complex is expected to behave as a complex ligand or a host molecule and form a polynuclear complex with other metal ions. Here, the binding ability of the boron complex toward lanthanoid ions (Ln), which have large coordination number and the flexible coordination structure, was studied by using UV–vis spectrophotometry.

Spectrophotometric titration of a $CHCl_3$ solution of the boron complex with a varying concentration of MeOH solution of LnA_36H_2O (A: Cl^-, NO_3^-) in the presence of triethylamine was carried out (Figure 1). The composition of the solution was kept constant at $CHCl_3$:MeOH = 4:1. Only the mixed solution of Ce became the brown colored solution. This general phenomenon

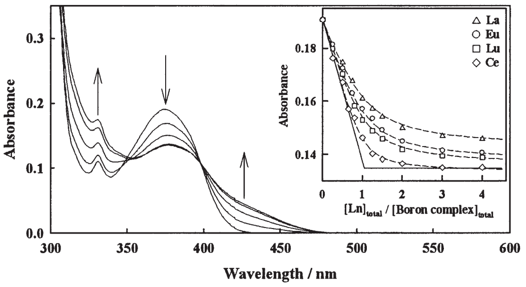


Figure 1. Absorption spectra of 1.4×10^{-5} M boron complex in the presence and absence of 3.5×10^{-6}–5.6×10^{-5} M $Ce(NO_3)_36H_2O$ in $CHCl_3$/MeOH solution. $[NEt_3] = 5.6 \times 10^{-5}$ M. Inset shows the molar ratio plots using the apparent absorbance at 375 nm.

indicates that Ce^{III} was oxidized to Ce^{IV} in the solution with the hydrolysis of Ce at neutral pH region.[8] Figure 1 demonstrates a clear isosbestic point at 398 nm, indicating an equilibrium system containing two chromophores, i.e., free boron complex and the boron complex captured a Ce ion (hetero-binuclear complex). Similar results were obtained for La, Eu, and Lu cases, although the wavelength of the isosbestic point were observed at 391 (La), 393 (Eu), and 394 nm (Lu) respectively. Inset shows the relationship between the absorption maximum of the boron complex at 375 nm and the molar ratio of Ln ion to the boron complex in the solution. The molar ratio plot of Ce obviously showed an intersection at the molar ratio of 1, which corresponds to a 1:1 stoichiometry as expected from an isosbestic point. Furthermore, the composition of the polynuclear complexes was supported by ESIMS measurements (cation mode): 1535, $[2L + B^{3+} + La(H_2O)_3{}^{3+} - 6H^+]H^+$; 1535, $[2L + B^{3+} + Ce(OH)(H_2O)_2{}^{3+} - 6H^+]H^+$; 1549, $[2L + B^{3+} + Eu(H_2O)_3{}^{3+} - 6H^+]H^+$; 1571, $[2L + B^{3+} + Lu(H_2O)_3{}^{3+} - 6H^+]H^+$. The binding constant, β_1 = [Binuclear complex]/([Boron complex][Ln]), determined by using the general equation derived with respect to the apparent absorbance (A_{app}) of the boron complex.[9] The logarithmic values of β_1 were calculated to be 4.42 ± 0.02 (La), 5.06 ± 0.01 (Ce), 4.55 ± 0.02 (Eu), 4.64 ± 0.02 (Lu) by a least-squares fitting for the plots in Figure 1 on the basis of the general equation. The dashed line in the inset of Fig. 1 indicate the regression curve, and is in good agreement with the experimental plots for all Ln.

IR spectrum (KBr) of the crude containing both free boron complex and the binuclear complex was measured. In all Ln cases, a clear band at 1640–1645 cm^{-1} which is significantly different from the stretching vibration of C=O (1680 cm^{-1}) in the free boron complex was observed. The C=O band observed in lower wavenumber region is similar to that of the Ln-methyl salicylate.[10] Therefore, a Ln ion is expected to be captured by the hydroxy groups at the end position, carbonyl groups in the methyl ester, and the negative charge of the boron complex as shown in Figure 2. Figure 3 shows the plot of the β_1 against the ionic potential of Ln ion (ionic charge/ionic radius). The β_1 value increased with increase the ionic potential, and a good correlation was observed. It was elucidated the stabilization of the hetero-binuclear complex strongly depends on the electrostatic interaction between the negatively charge of the boron complex and lanthanoid cation.

In conclusion, the complexation of the noncyclic ligand having plural hydroxy groups with boron proceeded selectively to afford a mononuclear complex. It has been found that the boron complex can act as a complex ligand and form a hetero-binuclear complex with a lanthanoid ion. Since various functionalized groups are introduced readily into the ester moiety in the ligand, the boron complexes having those ligands are expected to behave as a host molecule toward various metal cations, anions, and organic molecules. Furthermore, boron-assisted self-assembly of the functionalized ligands is possible to utilize the development of supramolecular structures such as helical compounds, rotaxanes, and catenanes.

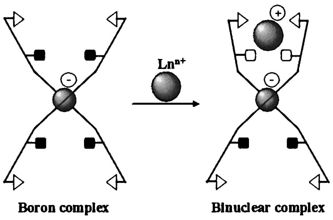


Figure 2. Complexation of the boron complex with a Ln ion. Coordinated water molecules or hydroxide ion of Ln ion were omitted for clarify. △: COOMe, ■: OH, □: O^-.

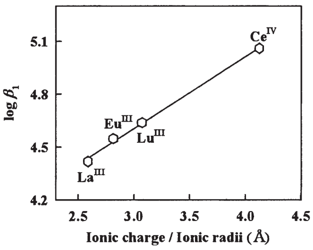


Figure 3. Correlation between the logarithmic values of the binding constant and the ionic potential of Ln ion. The ionic radii adopted the effective ionic radii in case of eight coordination.[11]

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6 Ligand **3**: 1HNMR ($CDCl_3$) δ 4.01 (s, 6H, –COOMe), 3.96 (s, 8H, Ar–CH_2), 4.54 (s, 2H, CH_2=C), 4.63 (s, 2H, CH_2=C), 7.26 (dd, 2H, Ar), 7.29 (t, 2H, Ar), 7.43 (t, 2H, Ar), 7.71 (d, 2H, Ar), 7.78 (d, 2H, Ar), 7.79 (dd, 2H, Ar), 8.42 (s, 2H, Ar), 6.09 (s, 2H, OH), 10.9 (s, 2H, OH). IR (KBr) 3430 cm^{-1} (O–H), 3211 (O–H), 1680 (C=O). ESIMS (CH_3CN) m/z = 669 (H^+).

7 Boron complex: 1HNMR ($CDCl_3$) δ 4.00 (s, 12H, –COOMe), 3.91 (s, 16H, Ar–CH_2), 4.39 (s, 4H, CH_2=C), 4.54 (s, 4H, CH_2=C), 7.14 (dd, 4H, Ar), 7.23 (t, 4H, Ar), 7.35 (t, 4H, Ar), 7.65 (dd, 4H, Ar), 7.73 (d, 4H, Ar), 8.38 (s, 4H, Ar), 10.7 (s, 4H, OH), 0.96 (t, 9H, NEt_3), 2.88 (q, 6H, NEt_3). IR (KBr) 3214 cm^{-1} (O–H), 1680 (C=O). Anal. Found(calcd.), C, 74.70(74.74); H, 5.72 (5.81); N, 0.90(0.97).

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9 $$A_{app} = \varepsilon\ [\text{Binuclear complex}] + \varepsilon_B\ [\text{Boron complex}]$$
$$= \left(\frac{(\beta_1 C_B + \beta_1 C_{Ln} + 1) - \sqrt{(\beta_1 C_B + \beta_1 C_{Ln} + 1)^2 - 4\beta_1{}^2 C_B C_{Ln}}}{2\beta_1}\right)$$
$$\times (\varepsilon - \varepsilon_B) + \varepsilon_B C_B$$
ε and ε_B denote the molar absorptivity of the binuclear complex and free boron complex, and C_B and C_{Ln} are the total concentration of the boron complex and Ln, respectively.

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