

## NMR Spectroscopic Evidence of Lewis Acid–Lewis Base Complex Formation of Perfluoroborane with Uranyl $\beta$ -Diketonato Complexes

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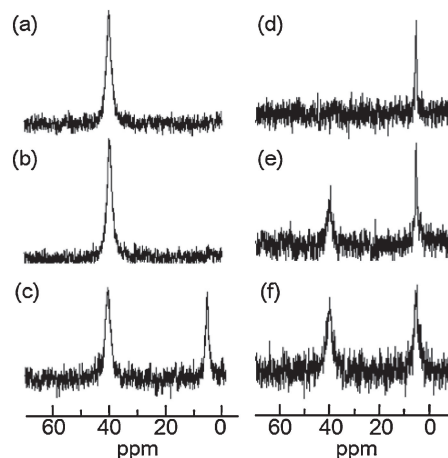
Interactions between  $B(C_6F_5)_2OH$  and  $[UO_2(dfh)_2(dmsO)]$  or  $[UO_2(acac)_2(dmsO)]$  in toluene have been investigated by  $^{11}B$ - and  $^{19}F$ NMR measurements. The results showed that one or two  $B(C_6F_5)_2OH$  molecules coordinate to the oxo ligands of  $[UO_2(acac)_2(dmsO)]$  through B, i.e.,  $O=U=O\cdots B$  (1:1) and  $B\cdots O=U=O\cdots B$  (2:1) complexes based on Lewis acid–Lewis base (LA–LB) interactions are formed, while such LA–LB interactions are not observed in  $[UO_2(dfh)_2(dmsO)]$ . Furthermore, it was clarified that the 2:1 complex becomes predominant with decreasing temperatures.

The functionalization of chemically inert two axial oxo ligands, so-called “yl” oxygen, of uranyl ion ( $UO_2^{2+}$ ) has attracted much attention in the fields of environmental radiochemistry, actinide chemistry, and geological disposal, because it plays an important role for understanding the chemical reactions of the uranyl moiety and the migration behavior of uranyl species in the environment.<sup>1–3</sup> Several studies have found that uranyl complexes with high Lewis basicity allow functionalization of the “yl” oxygens of  $UO_2^{2+}$ , and that the Lewis basic properties of “yl” oxygens can be enhanced by controlling the electron donicity of ligands in the equatorial plane. Examples of the functionalization include the exchange and scrambling reactions of “yl” oxygens.<sup>4–8</sup> Recently, unique Lewis acid–Lewis base (LA–LB) complexes, in which LA compounds can be directly coordinated to Lewis basic “yl” oxygens in uranyl complexes, have been synthesized and characterized using crystallographic and spectroscopic methods.<sup>2,3,9–16</sup> These studies have shown that alkali-, transition-, rare earth metals, and perfluoroarylborane are suitable as LA compounds.

However, such LA–LB uranyl complexes have been synthesized under limited coordination environments and isolated in the solid state. Hence, the knowledge about the interaction mechanisms in the formation of LA–LB uranyl complexes is limited, and especially little information is available concerning the interactions between LA compounds and “yl” oxygens of uranyl complexes in solutions.

In this study, we aimed to characterize the LA–LB interactions between bis(pentafluorophenyl)borinic acid ( $B(C_6F_5)_2OH$ ) and “yl” oxygens of uranyl  $\beta$ -diketonato complexes such as  $[UO_2(acac)_2(dmsO)]$  or  $[UO_2(dfh)_2(dmsO)]$  (dmsO: dimethyl sulfide, dfh: 4*H*,4*H*-decafluoroheptane-3,5-dionato, acac: acetylacetonato) in toluene and to examine their LA–LB complex formation equilibria by using  $^{11}B$  and  $^{19}F$ NMR measurements.

$B(C_6F_5)_2OH$  was synthesized through the hydrolysis of  $B(C_6F_5)_3$  as given in previous reports.<sup>17</sup> The  $^{11}B$ NMR spectra of toluene solution dissolved  $B(C_6F_5)_2OH$  ( $1.0$ – $5.0 \times 10^{-3}$  M, M: mol dm<sup>-3</sup>) and  $[UO_2(dfh)_2(dmsO)]$  ( $1.0 \times 10^{-3}$  M) were measured at 25 °C. As shown in Figures 1a and 1b, only one signal was observed at 40.0 ppm, and consistent with that of  $B(C_6F_5)_2OH$

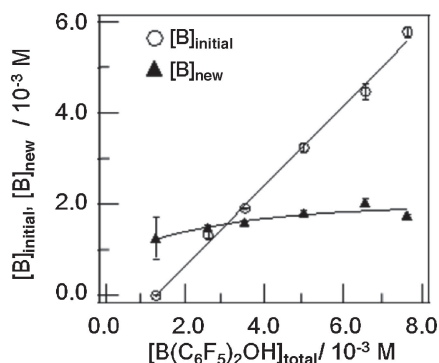


**Figure 1.**  $^{11}B$ NMR spectra of toluene solution dissolved  $B(C_6F_5)_2OH$  and  $[UO_2(dfh)_2(dmsO)]$  or  $[UO_2(acac)_2(dmsO)]$ . (a)  $[B(C_6F_5)_2OH] = 5.0 \times 10^{-3}$  M; (b)  $[B(C_6F_5)_2OH] = 5.0 \times 10^{-3}$  M,  $[UO_2(dfh)_2(dmsO)] = 1.0 \times 10^{-3}$  M; (c)  $[B(C_6F_5)_2OH] = 5.0 \times 10^{-3}$  M,  $[UO_2(acac)_2(dmsO)] = 1.0 \times 10^{-3}$  M; (d)  $[B(C_6F_5)_2OH] = 1.0 \times 10^{-3}$  M,  $[UO_2(acac)_2(dmsO)] = 1.0 \times 10^{-3}$  M; (e)  $[B(C_6F_5)_2OH] = 2.6 \times 10^{-3}$  M,  $[UO_2(acac)_2(dmsO)] = 1.0 \times 10^{-3}$  M; (f)  $[B(C_6F_5)_2OH] = 3.5 \times 10^{-3}$  M,  $[UO_2(acac)_2(dmsO)] = 1.0 \times 10^{-3}$  M.

itself in toluene. This result indicates that there are no apparent interactions between “yl” oxygens of  $[UO_2(dfh)_2(dmsO)]$  and  $B(C_6F_5)_2OH$  in toluene. This is considered to be due to the reduction of electron density of the “yl” oxygens with the electron-withdrawing effects of fluorine atoms of coordinated dfh.

In contrast, when  $[UO_2(acac)_2(dmsO)]$  ( $1.0 \times 10^{-3}$  M) was added into a toluene solution dissolving  $B(C_6F_5)_2OH$ , a new peak appeared around 5.0 ppm (Figure 1c). The area ratios of the peak at 40 ppm ( $\delta_{initial}$ ) to the new peak at 5 ppm ( $\delta_{new}$ ) were found to change with the variation of  $[B(C_6F_5)_2OH]$ . As seen from Figures 1d–1f, only  $\delta_{new}$  peak is observed in one equivalent of  $B(C_6F_5)_2OH$  to  $[UO_2(acac)_2(dmsO)]$  ( $[B(C_6F_5)_2OH]/[UO_2(acac)_2(dmsO)] = 1$ ), and the  $\delta_{initial}$  peak appears again and its relative intensity to  $\delta_{new}$  peak increases with increasing  $[B(C_6F_5)_2OH]$ . These results suggest that the  $\delta_{new}$  peak is attributed to the interaction of  $B(C_6F_5)_2OH$  with  $[UO_2(acac)_2(dmsO)]$ , because  $^{11}B$ NMR signals of B in oxo complexes such as  $[V\{OB(C_6F_5)_3\}(acac)_2]$ ,  $[Ti\{OB(C_6F_5)_3\}(acac)_2]$ ,  $cis\text{-}[MoO\{OB(C_6F_5)_3\}(acac)_2]$ , and  $[UO\{OB(C_6F_5)_3\}(NCN)_2]$  (NCN:  $\{(SiMe_3)CPh(NSiMe_3)\}$ ) are also observed at higher field than that of  $B(C_6F_5)_3$ .<sup>13,18</sup>

In order to determine the correct peak areas of  $\delta_{initial}$  and  $\delta_{new}$ , line shape fitting analyses based on Lorentz curves were performed. From the relative peak area ratios of  $\delta_{initial}$  to  $\delta_{new}$  (see Table S1 in the Supporting Information<sup>22</sup>) and the total concentrations of  $B(C_6F_5)_2OH$  ( $[B(C_6F_5)_2OH]_{total}$ ) in toluene

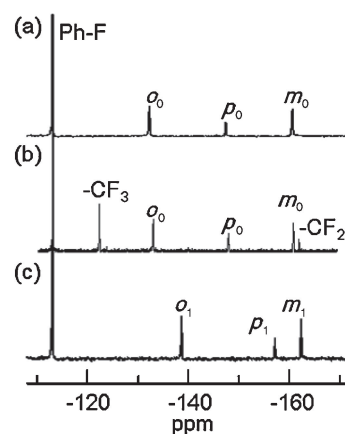


**Figure 2.** Plots of  $[B]_{\text{initial}}$  (○) and  $[B]_{\text{new}}$  (▲) against  $[B(C_6F_5)_2OH]_{\text{total}}$ . Error bars represent  $\sigma$  uncertainties.

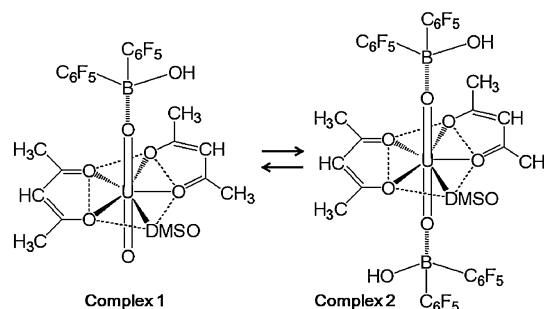
solutions, the  $B(C_6F_5)_2OH$  concentrations corresponding to  $\delta_{\text{new}}$  and  $\delta_{\text{initial}}$  ( $[B]_{\text{new}}$ ,  $[B]_{\text{initial}}$ ) were evaluated and plotted against  $[B(C_6F_5)_2OH]_{\text{total}}$  as shown in Figure 2. As seen from this figure, the  $[B]_{\text{initial}}$  values increase continuously from 0.0 to  $5.9 \times 10^{-3}$  M with increasing  $[B(C_6F_5)_2OH]_{\text{total}}$ , while the  $[B]_{\text{new}}$  values increase gradually from  $1.1 \times 10^{-3}$  M and approach a constant value, ca.  $2.0 \times 10^{-3}$  M. These results indicate that one and two equivalent  $B(C_6F_5)_2OH$  molecules interact with “yl” oxygens of  $[UO_2(acac)_2(dmsO)]$ , i.e., LA  $B(C_6F_5)_2OH$  molecules interact with LB “yl” oxygens of  $[UO_2(acac)_2(dmsO)]$  to form 1:1 ( $O=U=O \cdots B$ ) and 2:1 ( $B \cdots O=U=O \cdots B$ ) complexes in toluene. The existence of the interactions can be supported by infrared (IR) spectra of  $[UO_2(acac)_2(dmsO)]$ . The  $\nu_3$  peak corresponding to the  $O=U=O$  asymmetric stretching of  $[UO_2(acac)_2(dmsO)]$  was shifted from  $897$  to  $810$   $\text{cm}^{-1}$  by adding  $B(C_6F_5)_2OH$ , while this was not observed in the IR spectrum for  $[UO_2(dfh)_2(dmsO)]$  (Figure S1<sup>22</sup>).

When such specific LA–LB interactions exist,  $^{19}\text{F}$  NMR spectra of  $C_6F_5$  groups in  $B(C_6F_5)_2OH$  coordinated to  $[UO_2(acac)_2(dmsO)]$  should be also shifted toward higher field, because of fluorine shielding accompanied by the enhanced electron densities of the  $B \cdots O=U$  bond axis.<sup>19–21</sup> In particular, the *ortho* position of the  $C_6F_5$  groups should be most affected by the LA–LB interactions. Therefore, we measured  $^{19}\text{F}$  NMR spectra of toluene solution dissolved  $B(C_6F_5)_2OH$  and  $[UO_2(dfh)_2(dmsO)]$  or  $[UO_2(acac)_2(dmsO)]$  at  $25$  °C. The  $^{19}\text{F}$  NMR signals corresponding to *ortho*, *para*, and *meta* positions (peak-0: shown as  $o_0$ ,  $p_0$ , and  $m_0$ ) of  $C_6F_5$  groups in  $B(C_6F_5)_2OH$  itself were detected at  $-133.1$ ,  $-148.1$ , and  $-161.2$  ppm, respectively (Figure 3a). In the solution system containing  $B(C_6F_5)_2OH$  and  $[UO_2(dfh)_2(dmsO)]$ , the corresponding  $^{19}\text{F}$  NMR spectra were found to be observed at the same chemical shifts (Figure 3b), indicating that there were no  $B(C_6F_5)_2OH$ – $[UO_2(dfh)_2(dmsO)]$  interactions.

On the other hand, as expected, in the case of toluene solution dissolved  $[UO_2(acac)_2(dmsO)]$  ( $1.0 \times 10^{-3}$  M) and  $B(C_6F_5)_2OH$  ( $1.0 \times 10^{-3}$  M), the peaks corresponding *o*, *p*, and *m* positions (peak-1: shown as  $o_1$ ,  $p_1$ , and  $m_1$ ) were observed at  $-139.6$ ,  $-158.2$ , and  $-163.4$  ppm at higher fields than each position in peak-0 in Figure 3c. The difference between  $p_1$  and  $m_1$  was found to decrease from  $13.2$  to  $5.2$  ppm by adding  $[UO_2(acac)_2(dmsO)]$ . These observations are in good agreement with the case of LA–LB interactions between  $B(C_6F_5)_3$  and oxygen of water.<sup>19–21</sup> These results indicate that the  $o_1$ ,  $p_1$ , and  $m_1$  peaks are assigned as *ortho*, *para*, and *meta* positions of  $C_6F_5$ – groups in one  $B(C_6F_5)_2OH$  coordinated to one “yl” oxygen of  $[UO_2(acac)_2(dmsO)]$ ,



**Figure 3.**  $^{19}\text{F}$  NMR spectra of toluene solutions dissolved  $B(C_6F_5)_2OH$  and  $[UO_2(dfh)_2(dmsO)]$  or  $[UO_2(acac)_2(dmsO)]$ . (a)  $[B(C_6F_5)_2OH] = 2.5 \times 10^{-3}$  M; (b)  $[B(C_6F_5)_2OH] = 2.5 \times 10^{-3}$  M,  $[[UO_2(dfh)_2(dmsO)]] = 1.0 \times 10^{-3}$  M; (c)  $[B(C_6F_5)_2OH] = 1.0 \times 10^{-3}$  M,  $[[UO_2(acac)_2(dmsO)]] = 1.0 \times 10^{-3}$  M.

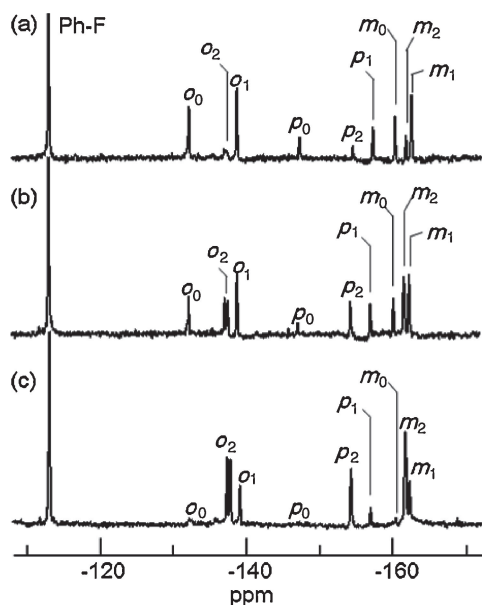


**Scheme 1.** Schematic illustrations of complexes 1 and 2.

i.e., the formation of 1:1 LA–LB complex of  $B(C_6F_5)_2OH$  with  $[UO_2(acac)_2(dmsO)]$  (complex 1 as illustrated in Scheme 1).

By adding almost two equivalents of  $B(C_6F_5)_2OH$  to  $[UO_2(acac)_2(dmsO)]$  ( $[B(C_6F_5)_2OH]/[[UO_2(acac)_2(dmsO)]] = 2.2$ ), the peak-0 appeared again and new peaks were observed at  $-138.1$ ,  $-155.5$ , and  $-162.7$  ppm (peak-2: shown as  $o_2$ ,  $p_2$ , and  $m_2$ ) as seen from Figure 4a. We found that the area ratios of peak-0, peak-1, and peak-2 are changed with an increase in  $[B(C_6F_5)_2OH]$ . In particular, the peak areas of peak-2 increased with increasing  $[B(C_6F_5)_2OH]$  and became larger than those of the peak-1 in excess  $[B(C_6F_5)_2OH] = 4.5 \times 10^{-3}$  M. This suggests that the peak-2 is assigned as  $C_6F_5$ – groups in 2:1 complex illustrated in complex 2 (Scheme 1), and that the 1:1 and 2:1 complexes coexist at equilibrium.

In order to confirm our above suggestion, temperature dependence of the  $^{19}\text{F}$  NMR spectra of toluene solution dissolved  $[UO_2(acac)_2(dmsO)]$  ( $1.0 \times 10^{-3}$  M) and  $B(C_6F_5)_2OH$  ( $0.5$ – $4.5 \times 10^{-3}$  M) was examined in the range from  $-30$  to  $25$  °C. In the case of less than one equivalent of  $[B(C_6F_5)_2OH]$  ( $0.5$ – $1.0 \times 10^{-3}$  M) to  $[UO_2(acac)_2(dmsO)]$ , the areas of peak-1 were almost constant without depending on the temperatures (Figure S2<sup>22</sup>). However, the peak area ratios were changed with decreasing temperature in the samples more than two equivalent of  $[B(C_6F_5)_2OH]$  ( $2.2$ – $4.5 \times 10^{-3}$  M) to  $[[UO_2(acac)_2(dmsO)]]$ . As shown in Figures 4a–4c, with decreasing temperatures the intensities of peak-2 increased with a decrease in those of peak-1 and only  $o_2$  peak



**Figure 4.**  $^{19}\text{F}$  NMR spectra of toluene solution dissolved  $\text{B}(\text{C}_6\text{F}_5)_2\text{OH}$  ( $2.2 \times 10^{-3}$  M) and  $[\text{UO}_2(\text{acac})_2(\text{dmsO})]$  ( $1.0 \times 10^{-3}$  M) measured at (a) 25, (b) 0, and (c)  $-30^\circ\text{C}$ .

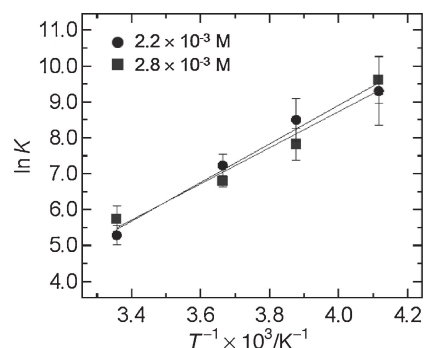
was split into two peaks. Furthermore, the peak-1 was completely disappeared at  $[\text{B}(\text{C}_6\text{F}_5)_2\text{OH}] = 4.5 \times 10^{-3}$  M and  $-30^\circ\text{C}$  (Figure S1<sup>22</sup>). These results indicate that the equilibrium between 1:1 and 2:1 complex shifts with the changes of  $[\text{B}(\text{C}_6\text{F}_5)_2\text{OH}]$  and temperatures.

Therefore, the areas of peak-0, peak-1, and peak-2 in the toluene solution dissolved  $\text{B}(\text{C}_6\text{F}_5)_2\text{OH}$  ( $2.2 \times 10^{-3}$  and  $2.8 \times 10^{-3}$  M) and  $[\text{UO}_2(\text{acac})_2(\text{dmsO})]$  ( $1.0 \times 10^{-3}$  M) were examined using line shape fitting, and their relative area ratios to the peak area of fluorobenzene (Ph-F,  $-113.0$  ppm) were determined. The relative area ratios were converted to  $[\text{B}(\text{C}_6\text{F}_5)_2\text{OH}]$  corresponding to each *o*, *p*, and *m* peak in the peak-0, peak-1, and peak-2 ( $[\text{B}_0]$ ,  $[\text{B}_1]$ , and  $[\text{B}_2]$ ) as listed in Table S2.<sup>22</sup> Based on these data, the equilibrium constants (*K*) between 2:1 and 1:1 complexes were evaluated by the following relation;

$$K = \frac{[\text{B}_2]/2}{[\text{B}_1][\text{B}_0]} \quad (1)$$

The *K* values for the systems of  $[\text{B}(\text{C}_6\text{F}_5)_2\text{OH}] = 2.2 \times 10^{-3}$  and  $2.8 \times 10^{-3}$  M were obtained respectively as  $(2.0 \pm 0.3) \times 10^2$  at  $25^\circ\text{C}$ ,  $(1.4 \pm 0.3) \times 10^3$  at  $0^\circ\text{C}$ ,  $(5.0 \pm 1.5) \times 10^3$  at  $-15^\circ\text{C}$ , and  $(1.1 \pm 0.7) \times 10^4$  at  $-30^\circ\text{C}$ , and  $(3.1 \pm 0.6) \times 10^2$  at  $25^\circ\text{C}$ ,  $(9.0 \pm 0.8) \times 10^2$  at  $0^\circ\text{C}$ ,  $(2.5 \pm 0.7) \times 10^3$  at  $-15^\circ\text{C}$ , and  $(1.5 \pm 0.5) \times 10^4 \text{M}^{-1}$  at  $-30^\circ\text{C}$ .

Furthermore, in order to evaluate the thermodynamic parameters, enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ), the  $\ln K$  values were plotted against the reciprocal temperature. As seen from Figure 5, both plots show the almost same linear relationships without depending on  $[\text{B}(\text{C}_6\text{F}_5)_2\text{OH}]$ . The  $\Delta H$  and  $\Delta S$  values were  $-44.7 \pm 4.2 \text{ kJ mol}^{-1}$  and  $-104.7 \pm 16.0 \text{ J mol}^{-1} \text{ K}^{-1}$  for  $[\text{B}(\text{C}_6\text{F}_5)_2\text{OH}] = 2.2 \times 10^{-3}$  M, and  $-41.8 \pm 5.7 \text{ kJ mol}^{-1}$  and  $-94.6 \pm 21.4 \text{ J mol}^{-1} \text{ K}^{-1}$  for  $[\text{B}(\text{C}_6\text{F}_5)_2\text{OH}] = 2.8 \times 10^{-3}$  M, respectively. The average values of  $\Delta H$  and  $\Delta S$  were determined to be  $-43.3 \pm 5.0 \text{ kJ mol}^{-1}$  and  $-99.7 \pm 18.7 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively. The negatively large  $\Delta H$  and  $\Delta S$  values indicate that the 2:1



**Figure 5.** Plots of  $\ln K$  vs. the reciprocal temperature for the equilibrium between 2:1 and 1:1 complexes. Error bars represent  $\sigma$  uncertainties.

complex is energetically more favorable and structurally more stable compared with the 1:1 complex.

From these results, it is concluded that the 1:1 and 2:1 LA-LB complexes consisting of  $\text{B}(\text{C}_6\text{F}_5)_2\text{OH}$  and  $[\text{UO}_2(\text{acac})_2(\text{dmsO})]$  are formed in toluene, and that the equilibrium for the LA-LB complex formation shifts to the direction of formation of the 2:1 complex with increasing  $[\text{B}(\text{C}_6\text{F}_5)_2\text{OH}]$  and decreasing temperatures.

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