Letters to the Editor

Macrocyclic structures of associated complexes of lithium tetraalkylborates

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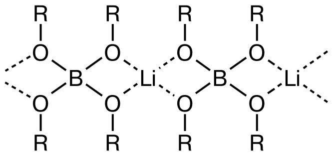
Based on the results of rheological study of structured solutions of lithium tetraalkylborates in hydrocarbons, it has been hypothesized[1] that the complexes are coordinated in an intermolecular fashion through Li...O bonds to form linear associates.



More recently, a study by mass spectrometry demonstrated[2] that associates formed by the [Bu^{t}OB(OR)$_3$]Li complexes (R = n-C$_3$H$_7$—n-C$_5$H$_{11}$) are no larger than tetramers regardless of the length of the R group, although the instrumental conditions allow the detection of the ion mass corresponding, for example, to the hexamer of the complex with R = Pr^n. The degree of association of the complexes depending on the size of the R group was estimated by small-angle X-ray scattering.[3] These experimental data led to a new hypothesis that the complexes are associated through the Li...O bonds to form a macrocyclic structure (Fig. 1, *a*). To establish the structure of associates, the [Bu^{t}OB(OR)$_3$]Li·mHOR complexes (R = Bu^n, n-C$_7$H$_{15}$, n-C$_{10}$H$_{21}$, or n-C$_{13}$H$_{27}$; m = 0—2) in heptane and cyclohexane-d$_{12}$ (concentrations were 0.03—0.07 mol L^{-1}) at 22 °C were studied by ^{7}Li and ^{11}B NMR spectroscopy on a JEOL FX-90 Q spectrometer. The chemical shifts (Table 1) were determined relative to LiCl, Bu^{t}OLi, and B(OH)$_3$ as the standards. The NMR spectra of all complexes have one narrow ^{7}Li signal at δ –1.1 and one narrow ^{11}B signal at δ –17.4. In the

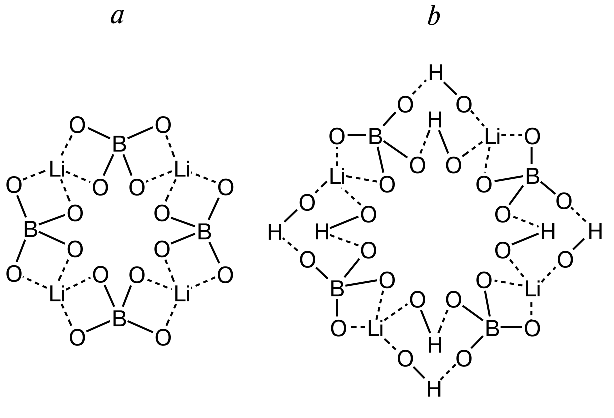


Fig. 1. Schematic representation of the structure of associated lithium tetraalkylborate (*a*) and its alcohol solvate (*b*).

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Table 1. NMR spectra of complexes

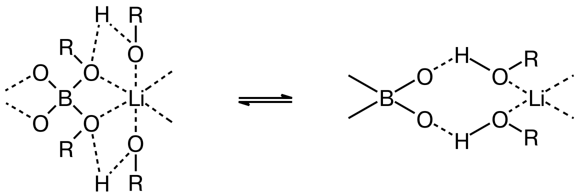
Complex	−δ	
	^{7}Li	^{11}B
[Bu^{t}OB(OBu^n)$_3$]Li	1.2	17.4
[Bu^{t}OB(OC$_7$H$_{15}$)$_3$]Li	1.1	17.4
[Bu^{t}OB(OC$_{10}$H$_{21}$)$_3$]Li	1.1	17.5
[Bu^{t}OB(OC$_{13}$H$_{27}$)$_3$]Li	1.1	17.4
[Bu^{t}OB(OC$_7$H$_{15}$)$_3$]Li • 2HOC$_7$H$_{15}$	1.35	17.4
[Bu^{t}OB(OC$_{10}$H$_{21}$)$_3$]Li • HOC$_{10}$H$_{21}$	1.35	17.4
B(OC$_8$H$_{17}$)$_3$	—	2.5

spectra of the solvated complexes, the only ^{7}Li signal is slightly broadened and is shifted to δ −1.35, neither the position nor the shape of the ^{11}B signal being changed. The NMR spectra show that all ^{7}Li and ^{11}B nuclei in associates of the complexes and their solvates are magnetically equivalent. This fact unambiguously confirms the macrocyclic structure of the associated complexes. In the case of linear association, the spectra of the [Bu^{t}OB(OR)$_3$]Li complexes should have at least two ^{7}Li signals and, presumably, two ^{11}B signals, because the terminal Li atoms with a coordination number of 2 are magnetically nonequivalent to the four-coordinate bridging Li atoms. Analogously, the terminal Li atoms with a coordination number of 4 in the spectra of the linearly associated [Bu^{t}OB(OR)$_3$]Li • 2HOR solvates are nonequivalent to the bridging six-coordinate Li atoms.

The macrocyclic structure of the associated complexes (see Fig. 1) is also supported by other experimental data. For example, the complexes are solvated by at most two moles of molecular oxygen or two moles of alcohol per Li atom.[4,5] The viscosity of the solution changes depending on the complex : alcohol ratio and has a maximum value at 1 : 2.[6] In the case of a linear structure, the complex should be coordinated by more than two moles of the solvating agent to achieve complete coordination saturation of the terminal Li atoms.

The IR spectra of the solvated complexes in CCl$_4$ show a broad band at 3095—3065 cm^{-1}, whose intensity increases substantially with increasing molar fraction of ROH and with increasing time of the reaction of alcohol with the complex, whereas the intensity of the absorption band belonging to the free OH group (3648—3632 cm^{-1}) decreases. The intensity of the band at 3095—3065 cm^{-1} varies depending on the degree of solvation of the complex analogously to the change in the viscosity of the solution. The addition of alcohol to a solution of the complex (more than two moles per Li atom) leads to a sharp decrease in both the intensity of this band and the viscosity of the solution. The presence of excess alcohol leads to destruction of the associated complexes. It is known that the absorption band of the coordinated OH group is shifted to lower frequencies with increasing size of the H-bonded ring.[7] The IR spectroscopic data indicate that the six-coordinate strained state of the Li atom changes to the more stable four-coordinate state in the solvate due to the intramolecular ring expansion in each monomer of the polyassociate (see Fig. 1, *b*) according to Scheme 1.

Scheme 1



In the presence of the complexes, water-free LiCl is dissolved in heptane, which qualitatively confirms the macrocyclic structure of the associated complexes and characterizes these associates as a new class of crown-ether analogs.

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