NMR Spectra of Guest–Host Complexes of Boron and Silicon Fluorides with Crown Ethers in Nonaqueous Solutions

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Abstract—¹⁹F, ¹¹B, and ²⁹Si NMR spectroscopy was used to examine the behavior of the guest–host complexes $(BF_3 \cdot H_2O)_2 \cdot 18$ -crown-6 $\cdot 2H_2O$, $(BF_3 \cdot H_2O)_2 \cdot DCH$ -6B, and (DCH-6A $\cdot H_3O)SiF_5$ in acetone (DCH-6B and DCH-6A are the *cis-anti-cis-* and *cis-syn-cis-* isomers of dicyclohexano-18-crown-6, respectively). It was shown that molecular boron fluoride complexes undergo partial solvolysis in acetone to yield $BF_3 \cdot acetone$ as the main product; the ionic pentafluorosilicate complex does not experience significant solvolysis transformations.

The stabilization of the unstable monohydrate BF₃ · H₂O in the guest–host complex BF₃ · H₂O · 18C6 (18C6 = 18-crown-6) [1] has stimulated the development of new simplified methods (as compared to that proposed in [1]) for the synthesis of labile complexes of boron and silicon fluoride complexes with crown ethers, as well as the study of their structure and properties [2–7]. The chemistry of these compounds in the crystalline state is well understood, and its different aspects are described [1–7], whereas their behavior in nonaqueous solvents is still an open question. In this communication, we attempt to estimate the state of the complexes (BF₃ · H₂O)₂ · 18C6 · 2H₂O, (BF₃ · H₂O)₂ · DCH-6B, and [(DCH-6A · H₃O)SiF₅] in acetone using ¹⁹F, ¹¹B, and ²⁹Si NMR spectroscopy.

 $(BF_3 \cdot H_2O)_2 \cdot 18C6 \cdot 2H_2O (I), (BF_3 \cdot H_2O)_2 \cdot DCH-6B (II), and [(DCH-6A \cdot H_3O)SiF_5] (III) were synthesized as described in [4, 5, 6], respectively.$

¹⁹F (376.44 MHz), ¹¹B (128.37 MHz), and ²⁹Si (79.46 MHz) NMR spectra of saturated solutions of **I**– **III** in acetone-d₆ were recorded on a Bruker DRX-400 spectrometer at 273 K with CF₃COOD, BF₃ · OEt₂ and Me₄Si as the external standards; the ¹⁹F NMR shifts are referenced to CFCl₃.

¹⁹F, ¹¹B, and ²⁹Si shifts and their relative integrated intensities and assignments are given in the table. The ¹⁹F and ¹¹B signals for the solutions of complexes I and II appear in the characteristic range of tetracoordinated complexes of boron trifluoride [8]. Taking into account the obvious analogies between the spectral parameters of compounds I and II, as well as the data of [9], the spectra can be interpreted as follows. The most intense ¹⁹F signals in the highest magnetic field correspond to the initial complexes I and II, while the low-field ¹⁹F signals are due to the BF₃ · acetone complex, which is a product of solvolysis of guest-host compounds according to the scheme

$$(BF_3 \cdot H_2O)_2 \cdot L \cdot nH_2O + acetone$$
(1)

$$\implies$$
 BF₃ · acetone + H₃O[BF₃OH] + L + nH₂O

for L = 18C6, *n* = 2 and for L = DCH-6B, *n* = 0.

The least intense ¹⁹F signals in the lowest magnetic field may be assigned to an ionized $H_3O[BF_3OH]$ species whose formation is quite probable for $[H_2O] > [BF_3][8, 9]$ and can be stimulated by the presence in the equilibrium system (1) of crown ethers that are superior

¹⁹F, ¹¹B, and ²⁹Si NMR spectral parameters for complexes I– III in acetone

Complex	δ(¹⁹ F), ppm (intensity, %)	$\delta(^{11}B \text{ or }^{29}Si),$ ppm	Assignment
Ι	-152.22 (100)	-1.35	Ι
	-151.15 (25)		
	-150.72 (19)	-1.26	$BF_3 \cdot acetone$
	-150.65 (5)		
	-149.53 (3)	-1.15	H ₃ O[BF ₃ OH]
	-149.46 (0.7)		
II	-151.91 (100)	-1.62	Π
	-151.84 (25)		
	-150.51 (97)	-1.53	$BF_3 \cdot acetone$
	-150.44 (24)		
	-149.38 (0.5)	-1.37	H ₃ O[BF ₃ OH]
	-149.31 (0.1)		
ш	-138.40	-112.94	SiF_5^-

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to acetone in their proton-accepting capacity. Such an assignment is indirectly confirmed by the observed differences between the concentrations of the $H_3O[BF_3OH]$ complex in the solutions of I and II. The greater number of water molecules contained in compound I favors the formation of this complex. Each ¹⁹F signal is split into two components spaced by 0.07 ppm with an intensity ratio of ~ 1 : 4. This is a result of a $^{10}B-$ ¹¹B isotopic shift (the natural abundance of ¹⁰B isotopes is 18.83%, while that of ¹¹B is 81.17%) [9]; the signal from the ¹⁹F nuclei bound to ¹¹B appears in the higher magnetic field. The character of the ¹⁹F NMR spectra excludes BF₃-catalyzed aldol condensation of acetone in the solutions of compounds I and II [10], which gives, apart from other products, a BF₃ complex with mesitylene oxide (δ (¹⁹F) = -145.5 ppm).

The ¹⁹F NMR spectrum of a solution of complex **III** shows a singlet at $\delta(^{19}\text{F}) = -138.4$ ppm corresponding to the pentafluorosilicate anion [11]. In the available literature, the $\delta(^{29}\text{Si})$ values for SiF_5^- anion are lacking; however, the chemical shift of a singlet in the ²⁹Si NMR spectrum (-112.9 ppm) is very close to the published $\delta(^{29}\text{Si})$ values for pentacoordinated alkyl- and aryltetrafluorosilicates [RSiF₄]⁻ (-109.0 to -126.1 ppm) [12].

The SiF₅ anion is known to be stable only in solutions containing salts of rather large cations [13], and in this connection, our spectral data clearly indicate the presence of the initial pentafluorosilicate **III** in the solution, rather than its decomposition product, e.g., acetone-solvated ionic pair (H₃O)SiF₅. Note that the observed ¹⁹F, ¹¹B, ²⁹Si signals show no fine structure caused by ¹⁹F–¹¹B and ¹⁹F–²⁹Si spin–spin coupling, which suggests the intermolecular exchange of fluoride ligands in the solutions of **I**–**III** which is catalyzed by water molecules and hydroxonium ions [14].

Hence, based on the spectral data obtained, one can conclude that molecular complexes **I** and **II** undergo partial solvolysis in acetone, probably, because of the breakdown of the H-bonding systems stabilizing these complexes, while the ionic complex **III** remains virtually unaffected by solvolytic transformations.

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