

THE COMPLEXATION EQUILIBRIA OF CALCIUM ION IN ALL-FLUORINE ENVIRONMENT WITH OXYGEN-DONATING LIGANDS[#]

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Abstract

Calcium ion in $[(C_5Me_4Et)TiF_3]_4CaF_2$ **1** is capable of increasing its coordination number from eight to nine by binding an additional ligand. The complexation equilibria of **1** with ligands tetrahydrofuran (THF), dioxane (diox) and hexamethylphosphoramide (HMPA) have been studied by variable temperature ^{19}F NMR spectroscopy. The following ΔH and ΔS values for complexation reactions were found: $-22.8(5)$ kJ mol $^{-1}$ and $-70.4(3)$ J mol $^{-1}$ K $^{-1}$ (THF); $-22.7(8)$ kJ mol $^{-1}$ and $-67.9(5)$ J mol $^{-1}$ K $^{-1}$ (diox); $-25(1)$ kJ mol $^{-1}$ and $-56.3(6)$ J mol $^{-1}$ K $^{-1}$ (HMPA); respectively.

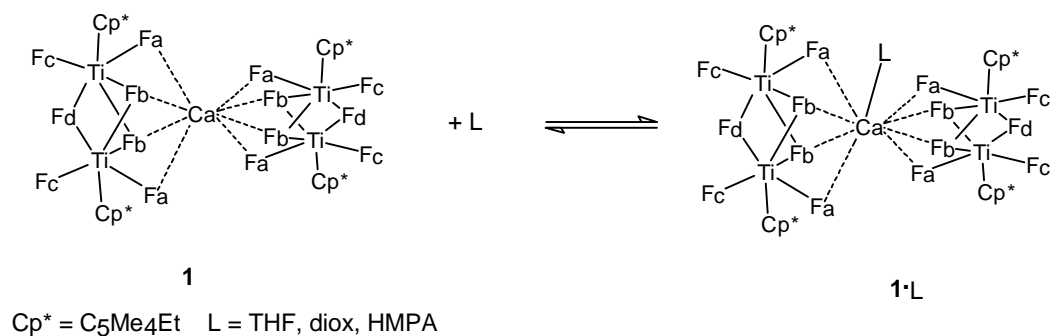
Introduction

The coordination chemistry of calcium is dominated by hard oxygen-donating ligands including small molecules as well as macrocyclic crown ethers and related ligands [1-3]. The most important small ligands are water, tetrahydrofuran and carboxylates. The exchange rate of complexation of aqua ligands on $Ca^{2+}(aq)$ in the range $6-9 \times 10^8$ s $^{-1}$ is in contrast to 5×10^5 s $^{-1}$ obtained for aqueous magnesium solutions [4]. The observed

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difference in lability of both ions is reflected in their biofunctions. Magnesium has largely a rigid structural role, the best known examples are Mg-porphyrin complex in photosynthesis and ATP-hydrolase. Calcium ion is more labile resembling sodium and potassium ions and plays a key role in dynamic processes such as neurotransmission and muscle contraction [5]. The comparison of structural parameters of Ca^{2+} -proteins and Ca^{2+} -small molecules interactions shows many similarities [5,6,7]. The study of complexation equilibria of Ca^{2+} with small molecules could therefore improve our understanding of dynamic Ca^{2+} -proteins processes.

Calcium ion in $[\{(\text{C}_5\text{Me}_4\text{Et})\text{TiF}_3\}_4\text{CaF}_2]$ **1** (Scheme 1) is coordinated by two tetradentate fluorine-donating $[(\text{C}_5\text{Me}_4\text{Et})_2\text{Ti}_2\text{F}_7]^-$ ligands and is capable of extension of coordination sphere by binding an additional ligand [8,9]. We isolated and determined the structure of **1**·HMPA (HMPA = hexamethylphosphoramide) with a nine-coordinated calcium ion. The variable temperature ^{19}F NMR spectroscopy was used to study the solvation of **1** [9]. In this paper, we present the study of equilibria of **1** with small ligands tetrahydrofurane, dioxane and hexamethylphosphoramide by use of ^{19}F and ^1H variable temperature spectroscopy (Scheme 1).



Scheme 1.

Experimental

The compound $[\{(\text{C}_5\text{Me}_4\text{Et})\text{TiF}_3\}_4\text{CaF}_2]$ **1** was prepared as previously reported [8]. Deuterated toluene (Aldrich) was dried with potassium and distilled under reduced pressure. The solid samples of **1** were weighed in a dry-box into NMR tubes and solvent and ligand were added in the counter-flow of dry argon. The following amounts of

substances were used in the preparation of NMR-samples: a) 12 mg of **1**, 1.20 mL of [²H₈]toluene, 26 mg of THF; b) 9 mg of **1**, 0.82 mL of [²H₈]toluene, 16 mg of diox; c) 11 mg of **1**, 0.72 mL of [²H₈]toluene, 5 mg of HMPA. The ¹H and ¹⁹F NMR spectra were recorded on a Bruker DPX 300 spectrometer and the respective nuclei chemical shifts referenced to external samples of SiMe₄ (¹H) and CFCl₃ (¹⁹F). Variable temperature spectra were recorded using the variable temperature controller of the spectrometer. The sample was allowed to equilibrate for at least 10 minutes before beginning the spectral acquisition.

Results and Discussion

The ¹⁹F NMR spectrum of [²H₈]toluene solution of **1** exhibits four resonances assigned to the following fluorine atoms (in the order of increasing shielding, see also Scheme 1): terminal (F_c), doubly bridging (F_a), doubly bridging (F_d) and triply bridging (F_b) [9]. A new set of fluorine resonances appears along the resonances of **1**, when THF, diox or HMPA were added (Figures 1-3). The new resonances are ascribed to the complex **1**·L (L = THF, diox, HMPA). The ratio of intensities of **1** and **1**·L is temperature dependent, suggesting the equilibria shown in Scheme 1. The resonances of F_c and F_a fluorines were used in order to calculate the equilibrium constants:

$$K = C_{1\cdot L} / (C_1 \cdot C_L)$$

The resonances of fluorine atoms F_b and F_d (not shown in Figures 1-3) of **1** and **1**·L were not used in equilibrium constant calculations due to overlapping. The plot of ln *K* versus 1/*T* (Figure 4) gave the enthalpy and entropy changes for the complexation of **1**. The following Δ*H* and Δ*S* values for complexation reactions (Scheme 1) were found: -22.8(5) kJ mol⁻¹ and -70.4(3) J mol⁻¹ K⁻¹ (L = THF), -22.7(8) kJ mol⁻¹ and -67.9(5) J mol⁻¹ K⁻¹ (L = diox), -25(1) kJ mol⁻¹ and -56.3(6) J mol⁻¹ K⁻¹ (L = HMPA); respectively. The negative values of Δ*H* and Δ*S* support the proposed reaction of binding of an additional ligand. The values of thermodynamic parameters for

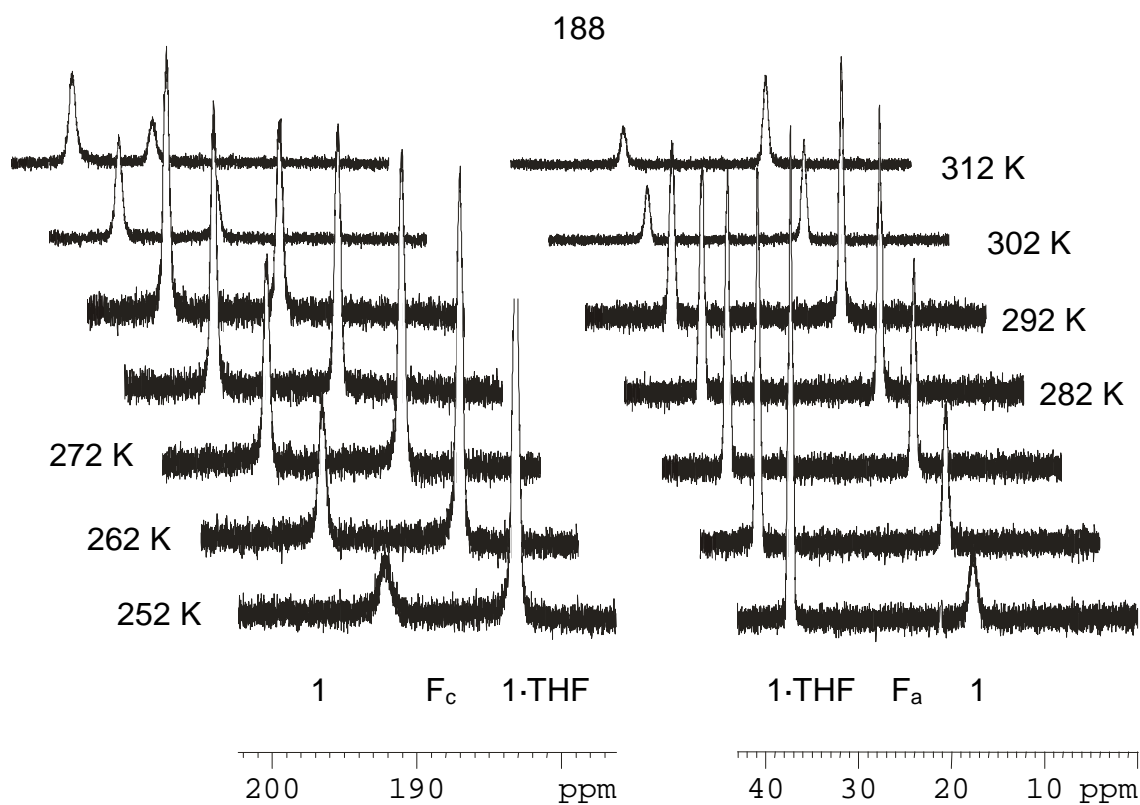


Figure 1. The variable temperature ^{19}F NMR spectra of **1** with added THF. See Scheme 1 for labels.

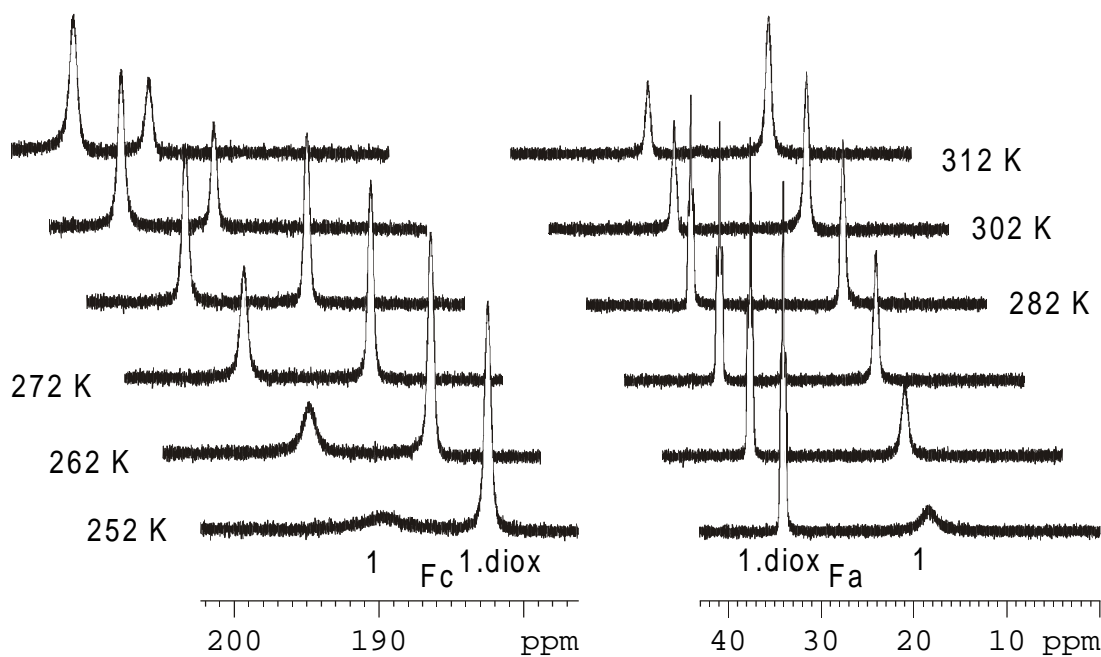


Figure 2. The variable temperature ^{19}F NMR spectra of **1** with added diox. See Scheme 1 for labels.

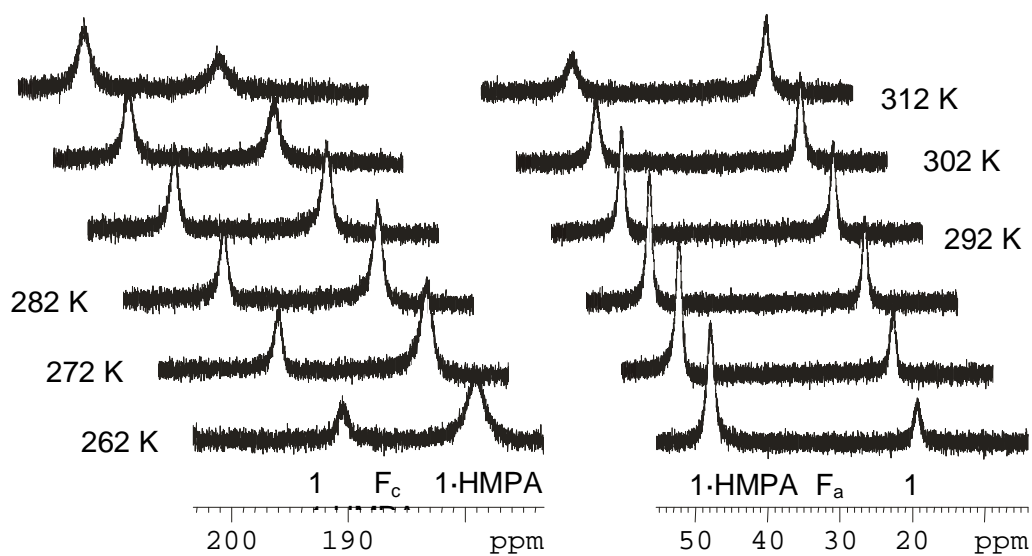


Figure 3. The variable temperature ^{19}F NMR spectra of **1** with added HMPA. See Scheme 1 for labels.

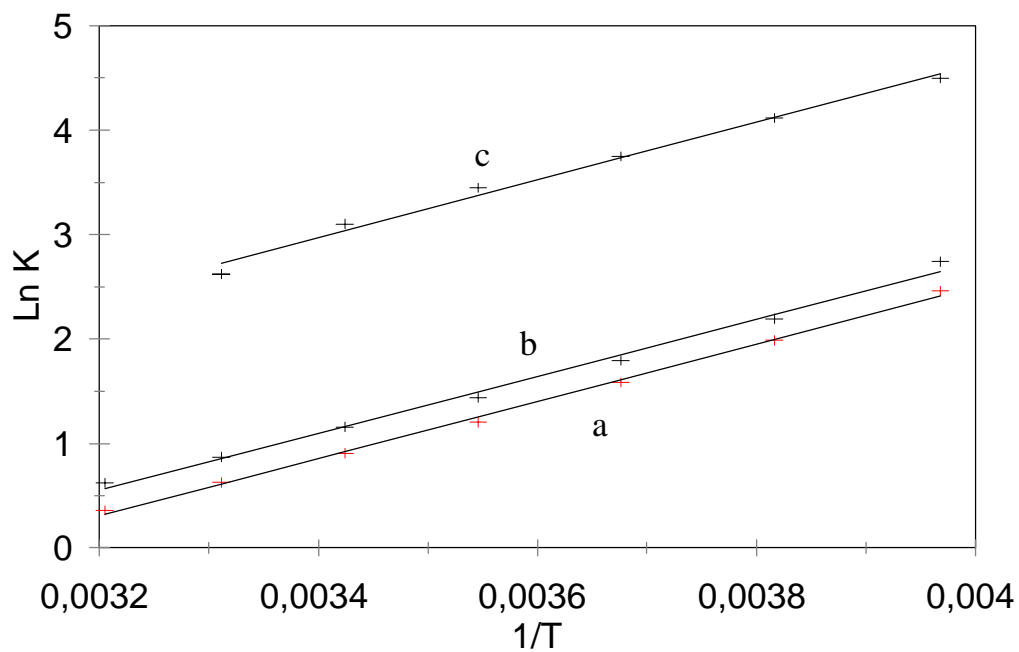


Figure 4. The temperature dependency of equilibrium constants for the complexation of **1** with THF (a), diox (b) and HMPA (c).

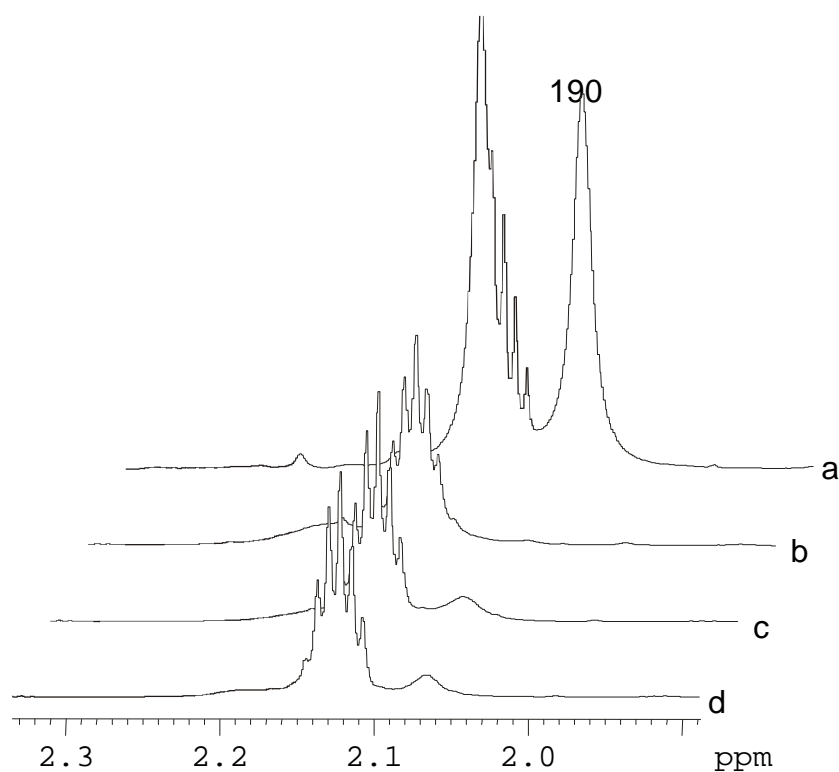


Figure 5. The ^1H NMR spectra ($\text{C}_5\text{Me}_4\text{Et}$ resonances) of **1** (a), **1** with added THF (b), **1** with added diox (c), **1** with added HMPA (d). The multiplet is the residual resonance of the solvent.

complexation with tetrahydrofuran and dioxane are very similar. Although the complexation constants of **1** with hexamethylphosphoramide are higher, they result in only about ten percent higher enthalpy change. The complexation of calcium ion with aqua ligands has been studied by *ab initio* methods [1, 10] and the calculation for the reaction: $[\text{Ca}(\text{H}_2\text{O})_8]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Ca}(\text{H}_2\text{O})_9]^{2+}$ resulted in enthalpy change of -57 kJ mol^{-1} [1]. On the other hand there is a lack of experimental results for the complexation of calcium ion with a single ligand.

The complexation and decomplexation reactions are not fast on the ^{19}F NMR timescale, since separate resonances were observed for each species. The ^1H NMR spectrum of **1** has two resonances of methyl protons of the organic ligand $\text{C}_5\text{Me}_4\text{Et}$. The intensity of the resonances decrease after addition of THF, diox or HMPA (Figure 5). A possible explanation is the coalescence due to complexation-decomplexation reaction

with the rate comparable to the ^1H NMR timescale. However, the line shape analysis that would result in the rate of reactions was not possible due to overlapping of **1**, **1**·L and residual solvent resonances.

Acknowledgements

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Povzetek

Kalcijev ion v spojini $[(\text{C}_3\text{Me}_4\text{Et})\text{TiF}_3]_4\text{CaF}_2$ **1** lahko veže dodatni ligand in tako poveča koordinacijsko število z osem na devet. S spreminjanjem temperature smo študirali ravnotežja kompleksacije spojine **1** z ligandi tetrahidrofuranom, dioksanom in heksametilfosforamidom. Ravnotežja smo opazovali z ^{19}F NMR spektroskopijo. Določili smo sledeče ^1H in ^1S vrednosti za reakcije vezave liganda: $-22.8(5)$ kJ mol $^{-1}$ in $-70.4(3)$ J mol $^{-1}$ K $^{-1}$ (tetrahidrofuran); $-22.7(8)$ kJ mol $^{-1}$ in $-67.9(5)$ J mol $^{-1}$ K $^{-1}$ (dioksan); $-25(1)$ kJ mol $^{-1}$ in $-56.3(6)$ J mol $^{-1}$ K $^{-1}$ (heksametilfosforamid).