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Investigation of the Cation Complexation by Macrocyclic Ethers using ^{13}C NMR Spin--Lattice Dipolar Relaxation Time Measurements

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Abstract: The binding constants (K_a) of [18]crown-6 ether with Na^+ , K^+, and Ba^{2+} thiocyanates were determined by $^{13}C\{^1H\}$ NMR spin--lattice dipolar relaxation time measurements. The observed relaxation times (T_{obs}) for ^{13}C nuclei are dependent upon the relaxation times of the complexed (T_{1a}) and free crown ether (T_{1f}), and were measured in [D4]methanol using inversion--recovery measurements in the extreme narrowing limit (75 MHz). The observed ^{13}C relaxation times of the metal complexes were found to be smaller than those of the cation-free macrocyclic ether due to reduced internal flexibility of the macrocycles in the complexes. The relationship $1/T_{obs} = P_a/T_{1a} + P_f/T_{1f}$ was used to estimate K_a for the n:m stoichiometry of the cation complexes in [D4]methanol and were found to run in the order $Ba^{2+} > K^+ > Na^+$. The T_1 measurements within the temperature range of 280--301 K yielded energy barriers for the internal interconversion of the --O--CH_2--CH_2--O-- structural fragments in free and complexed [18]crown-6 ether. The results indicated that the energy barriers of complexed crown ether are lower than those of the cation-free molecule, indicating the stabilization of preferred conformations in the cation-complexed crown ethers.

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