A Structural and Dynamic Study of Cryptates

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Contents

Summary

The crystal structures of the cryptate [Li.C21C5]NCS and the diaza crown ether complex [K.C21]NCS have been determined by X-ray crystallography. The structures are compared with structures of related cryptates and diaza crown complexes to afford an assessment of the effect of variation of the position and number of donor atoms in cryptands on the structure of alkali metal cryptates.

The complexation of Li^+ by the cryptand C21C5 has been studied in seven solvents by ^7Li nmr spectroscopy and potentiometric titration. The stability constants $\log\{K_s/dm^3\ mol^{-1}\}$ values at 298.2 K, for $[Li.C21C5]^+$ and $[Ag.C21C5]^+$ respectively are: in acetonitrile (4.15, 4.29), methanol (3.01, 7.69), dimethylformamide (1.80, 5.23), dimethylacetamide (1.85, 4.45), and diethylformamide (1.72, 4.95). The Li^+ exchange on the $[Li.C21C5]^+$ is in the very slow regime of the ^7Li nmr timescale in acetonitrile, propylene carbonate, and acetone, and within the ^7Li nmr timescale in methanol, dimethylformamide, dimethylacetamide, and diethylformamide. Thus the respective decomplexation rate constants obtained from subsequent lineshape analysis are k_d (298.2 K) = 21.6 ± 0.4, 116 ± 2, 237 ± 4, and 210 ± 4 s^{-1} The corresponding activation parameters are $\Delta H^{\ddagger}$ = 36.1 ± 0.9, 38.4 ± 0.9, 49.0 ± 2.1, and 27.8 ± 1.5 kJ mol^{-1} and $\Delta S^{\ddagger}$ = -98.4 ± 3.1, -76.5 ± 3.0, -35.0 ± 2.8, and -108 ± 5 J K^{-1} mol^{-1}. The variation of the ^{13}C and ^7Li chemical shifts of $[Li.C21C5]^+$ with solvent is employed in a structural investigation of this cryptate in solution. The equilibrium and kinetic data are discussed in conjunction with data from other related cryptates.

Complexation of Na^+ by the closely related ligands C21, C211 and $C21C_5$ has been studied by ^{23}Na nmr spectroscopy and potentiometric titration. The stability constants $\log\{K_s/dm^3\ mol^{-1}\}$ values at 298.2 K for $[Na.C21]^+$ in the three solvents dimethylformamide, dimethylacetamide and diethyformamide (of similar electron donating strength but different molecular size) are 2.10, 2.88 and 3.19 respectively. The $\log\{K_s/dm^3\ mol^{-1}\}$ values at 298.2 K, for $[Na.C21C_5]^+$ and $[Na.C211]^+$ respectively are: in dimethylacetamide (2.05, 4.74), and in diethylformamide (2.52, 5.10). The Na^+ exchange on the $[Na.C21C_5]^+$ is in the very fast regime of the ^{23}Na nmr timescale in dimetylacetamide and diethylformamide. The Na^+ exchange on the $[Na.C211]^+$ is within the ^{23}Na nmr timescale in diethylformamide. Thus the decomplexation rate constant obtained is k_d (298.2 K) = 18.2 ± 2.0 s^{-1} and the corresponding activation parameters are $\Delta H^{\neq}$ = 67.1 ± 1.9 kJ mol^{-1} and $\Delta S^{\neq}$ = 4.4 ± 5.0 J K^{-1} mol^{-1}. These data are compared with each other and with similar complexes in the light of ligand and solvent molecular characteristics.

Complexation of Li^+ and Ag^+ by the clam-like cryptand $C22C_2$ has been studied in seven solvents by ^7Li nmr spectroscopy and potentiometric titration. The stability constants $\log\{K_s/dm^3\ mol^{-1}\}$ values at 298.2 K, for $[Li.C22C_2]^+$ and $[Ag.C22C_2]^+$ respectively are: in acetonitrile (7.8, 9.4), acetone (8.9, 13.1), water (<2, 6.0), methanol (4.0, 10.2), dimethylformamide (3.5, 9.4), diethylformamide (3.1, 8.2), and pyridine (4.0, 5.0). The Li^+ exchange on the $[Li.C22C_2]^+$ is in the very slow regime of the ^7Li nmr timescale in acetonitrile, acetone and pyridine, in the very fast regime in water, and within the ^7Li nmr timescale in methanol, dimethylformamide and diethylformamide. Thus the respective decomplexation rate constants obtained are k_d

(298.2 K) = 971 ± 42, 240 ± 7, and 916 ± 28 s^{-1}. The corresponding activation parameters are $\Delta H^{\neq}$ = 31.0 ± 0.4, 22.5 ± 1.2 and 26.7 ± 0.6 kJ mol^{-1} and $\Delta S^{\neq}$ = -84.0 ± 2.6, -124 ± 5 and -98.6 ± 2.3 J K^{-1} mol^{-1}. These data are discussed in the context of the effects of cryptand structure and solvent characteristics on cryptate lability and stability.