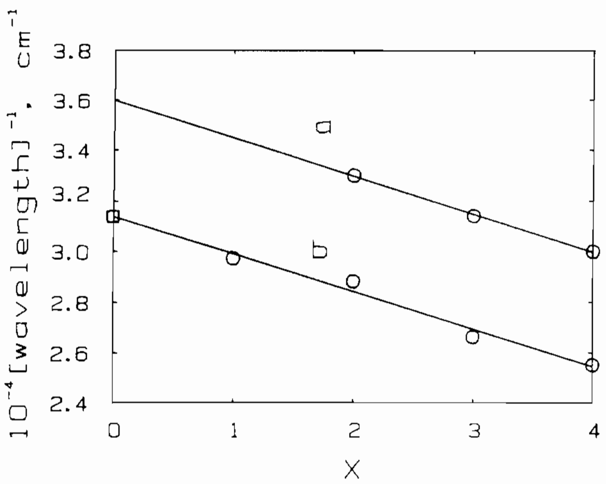


Figure 9. Linear relationships between $1/\lambda_{max}$ of Pt(II) complexes and number of chloride ions in the complex: (a) $d_{xz,yz} \rightarrow d_{x^2-y^2}$ transition (slope = $-(1.49 \pm 0.04) \times 10^{-4}$ nm^{-1}, intercept = $(3.60 \pm 0.02) \times 10^{-3}$ nm^{-1}); (b) $d_{xy} \rightarrow d_{x^2-y^2}$ transition (slope = $-(1.5 \pm 0.2) \times 10^{-4}$ nm^{-1}, intercept = $(3.13 \pm 0.05) \times 10^{-3}$ nm^{-1}).

larger ϵ values for this transition, while the ϵ values for the $d_{xy} \rightarrow d_{x^2-y^2}$ band change very little.

The law of average environment states that the crystal field Δ value for a mixed-ligand octahedral complex is given by the weighted average of the Δ values for each of the individual ligands.[39] We find that a similar relationship exists for the square-planar complexes. Plots of the reciprocals of λ_{max} of the $PtCl_x(OH)_{4-x}^{2-}$ complexes vs x (the number of chloride ions coordinated to Pt(II)) give straight lines (Figure 9) for both absorption bands. The plot of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition has an intercept of 3.60×10^{-3} nm^{-1}, and that of the $d_{xz,yz} \rightarrow d_{x^2-y^2}$ transition, 3.13×10^{-3} nm^{-1}. The latter is seen as a shoulder at 320 nm in the resolved spectrum of $Pt(OH)_4^{2-}$. The correlation predicts another d–d transition for $Pt(OH)_4^{2-}$ at 278 nm, but the intense charge-transfer bands below 250 nm mask this absorption band.

Acknowledgment. This work was supported by Public Health Service Grant No. GM12152 from the National Institute of General Medical Sciences. We are grateful to Robert E. Santini for his assistance in the NMR experiments.

Appendix. Validity of Assignment of Reaction Times for the ^{195}Pt NMR Kinetic Data

For the ^{195}Pt NMR data used in the evaluation of the rate constants, the intensity of the signal, I_{exp}, was obtained from the integrated average over a 1-h period. The time assigned in this evaluation, t_{exp}, was the midpoint of the time interval. Since the actual time (t_{act}) when the intensity is equal to I_{exp} is not exactly at the midpoint, it is necessary to check the validity of using t_{exp} instead of t_{act}.

For a first-order reaction

$$I = I_0 e^{-kt} \tag{A1}$$

$$I_{exp} = 1/(t_2 - t_1) \int_{t_1}^{t_2} I \, dt = \frac{I_0}{k(t_2 - t_1)}(e^{-kt_1} - e^{-kt_2}) \tag{A2}$$

where t_1 and t_2 are the initial and final times used to obtain the signal.

When $t = t_{act}$

$$I_{exp} = I_{act} = I_0 e^{-kt_{act}} \tag{A3}$$

Equating eq A2 and eq A3 permits t_{act} to be evaluated:

$$t_{act} = -\frac{1}{k} \ln \left[\frac{e^{-kt_1} - e^{-kt_2}}{k(t_2 - t_1)} \right] \tag{A4}$$

When $t_1 = 1800$ s, $t_2 = 5400$ s, and $k = 7.2 \times 10^{-5}$ s^{-1}, eq A4 gives $t_{act} = 3561$ s. This is very close to the t_{exp} value used: $(t_1 + t_2)/2 = 3600$ s. Hence the experimental error in the time assignment is only 1% for the fastest rate and is less for other measurements.

---

(39) Sutton, D. *Electronic Spectra of Transition Metal Complexes*; McGraw-Hill: London, 1968; p 162.

Contribution from the Department of Physical and Inorganic Chemistry,
University of Adelaide, Adelaide, South Australia 5001, Australia

Complexation of Lithium Ion by the Cryptand 4,7,13-Trioxa-1,10-diazabicyclo[8.5.5]eicosane (C21C$_5$) in a Range of Solvents. A ^{7}Li Nuclear Magnetic Resonance and Potentiometric Titration Study

Stephen F. Lincoln* and Amira Abou-Hamdan

Received October 25, 1989

Complexation of Li$^+$ by the cryptand 4,7,13-trioxa-1,10-diazabicyclo[8.5.5]eicosane (C21C$_5$) to form the cryptate [Li.C21C$_5$]$^+$ has been studied in eight solvents by ^{7}Li NMR and potentiometric titration methods. The variation of the ^{7}Li chemical shift of [Li.C21C$_5$]$^+$ with solvent and a comparison of its stability with those of other cryptates indicate that [Li.C21C$_5$]$^+$ exists substantially in the *exclusive* form in solution in contrast to the *inclusive* form adopted in the solid state. The exchange of Li$^+$ on [Li.C21C$_5$]$^+$ is within the ^{7}Li NMR time scale in methanol, dimethylformamide, diethylformamide, and dimethylacetamide, where, in the last solvent at 298.2 K, the logarithm of the [Li.C21C$_5$]$^+$ stability constant [log (K/dm^3 mol^{-1})] is 1.85 and the decomplexation kinetic parameters are $k_d = 237 \pm 4$ s^{-1}, $\Delta H_d^* = 49.0 \pm 2.1$ kJ mol^{-1}, and $\Delta S_d^* = -35.0 \pm 2.8$ J K^{-1} mol^{-1}. Similar data are obtained in the other three solvents. In acetonitrile, propylene carbonate, and acetone, Li$^+$ exchange is too slow to be studied by ^{7}Li NMR spectroscopy. The [Li.C21C$_5$]$^+$ data are compared with those for [Li.C211]$^+$, [Na.C21C$_5$]$^+$, and [Na.C211]$^+$.

Introduction

Studies of the complexes, or cryptates, formed between alkali-metal ions and poly(oxadiazabicycloalkane) ligands, or cryptands, have produced a substantial understanding of the effects of metal ion size and cryptand cavity size on the structure, stability, and lability of cryptates, and the mechanisms of cryptate complexation processes.[1-16] Recently attention has turned to the effect of the cryptand donor atoms on these characteristics of the com-

---

(1) Lehn, J.-M. *Struct. Bonding (Berlin)* **1973**, *16*, 1-69.
(2) Lehn, J.-M. *Acc. Chem. Res.* **1978**, *11*, 49-57.
(3) Lehn, J.-M. *J. Inclusion Phenom.* **1988**, *6*, 351-396.

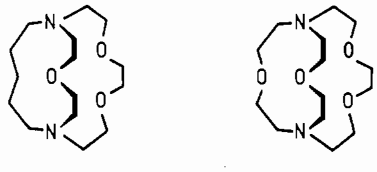
0020-1669/90/1329-3584$02.50/0 © 1990 American Chemical Society

Table I. Solution Compositions and ^{7}Li Chemical Shifts (280.1 K) for the [Li.C21C$_5$]$^+$ System

solvent	D_N[a]	[LiClO$_4$], mol dm^{-3}	[C21C$_5$], mol dm^{-3}	Li$^+$ solvated		[Li.C21C$_5$]$^+$		corr applied, ppm
				δ_{obs},[b] ppm	δ_{cor},[c] ppm	δ_{obs},[b] ppm	δ_{cor},[c] ppm	
acetonitrile	14.1	0.0201	0.0110	0.52	−0.26	−1.37	−2.15	−0.78
propylene carbonate	15.1	0.0197	0.0117	−0.29	−0.48	−0.04	−0.23	−0.19
acetone	17.0	0.0196	0.0116	2.10	1.02	0.81	−0.27	−1.08
water	18.1 (33)[d]	0.0189	0.0095	0.00	0.00	−0.216	−0.216	0
methanol	19.0 (23.5)[d]	0.0201	0.0108	0.04	−0.75	0.44	−0.35	−0.79
dimethylformamide	26.6	0.0199	0.0099	0.89	0.19	0.22	−0.48	−0.70
pyridine	33.1	0.0207	0.0103	2.31	1.86	−0.56	−1.01	−0.45

[a] Gutmann donor numbers from ref 23. [b] Chemical shifts referenced to a 0.005 mol dm^{-3} solution of LiClO$_4$ in water as external reference. A negative sign indicates an upfield shift. [c] Bulk diamagnetic susceptibility corrections made as described in Experimental Section. [d] These alternative D_N values have been proposed for aqueous and methanol solutions, respectively, in ref 24 and in: DeWitte, W. J.; Popov, A. I. *J. Soln. Chem.* **1976**, *5*, 231–240. The D_N values derived by Gutmann refer to dilute solutions of the solvents in 1,2-dichloroethane.

Chart I



C21C$_5$ C211

plexation process as exemplified by studies of (4,7,13-trioxa-1,10-diazabicyclo[8.5.5]eicosane)sodium(I) ([Na.C21C$_5$]$^+$) and the closely related (4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]-eicosane)sodium(I) ([Na.C211]$^+$) cryptate.[8,10-14] (It is seen in Chart I that C21C$_5$ differs from C211 by the replacement of an oxygen by a methylene group.) It is found that [Na.C21C$_5$]$^+$ is less stable than [Na.C211]$^+$ in a range of solvents, largely as a consequence of its greater rate of decomplexation.[13,14] In the solid state [Na.C21C$_5$]$^+$ and [Na.C211]$^+$ exist as *exclusive* cryptates, in which Na$^+$ resides outside the cryptand cavity and above the 15-membered rings of C21C$_5$ and C211 delineated by two nitrogens and three oxygens.[11] In contrast, [Li.C21C$_5$]$^+$ and [Li.C211]$^+$ exist as *inclusive* cryptates, where Li$^+$ resides in the cryptand cavities, in the solid state.[15,16] NMR studies indicate that [Li.C211]$^+$ largely retains its inclusive structure in several solvents,[4] but the solution chemistry of [Li.C21C$_5$]$^+$ has only been explored in a preliminary manner.[15,17] In this study the structure, stability, and lability of [Li.C21C$_5$]$^+$ are examined in a range of solvents to afford comparisons with [Li.C211]$^+$, [Na.C21C$_5$]$^+$, and [Na.C211]$^+$ and an improved understanding of the effect of the cryptand donor atom variation in these cryptates.

Experimental Section

The cryptand C21C$_5$ was prepared as described previously.[11] Lithium perchlorate (Fluka) was vacuum-dried at 353–363 K for 48 h and was stored over P$_2$O$_5$ under vacuum. Acetonitrile, methanol, propylene carbonate, acetone, dimethylformamide, diethylformamide, dimethylacetamide, and pyridine were purified and dried as described in the literature[18] and were stored under nitrogen over Linde 3A molecular sieves in the case of acetonitrile and methanol and over Linde 4A molecular sieves in the case of the other solvents. The water content of these solvents was below the Karl Fischer detection level of ca. 50 ppm. All solutions of LiClO$_4$ and C21C$_5$ were prepared under dry nitrogen in a glovebox.

For variable-temperature ^{7}Li NMR studies, solutions were sealed under vacuum in 5-mm NMR tubes that were coaxially mounted in 10-mm NMR tubes containing either D$_2$O, acetone-d_6, or dimethyl-d_6 sulfoxide, which provided the deuterium lock signal. For studies of the variation of ^{7}Li chemical shifts with the nature of the solvent, the sealed 5-mm NMR tubes were coaxially mounted in 10-mm NMR tubes containing 0.005 mol dm^{-3} LiClO$_4$ in 1/9 v/v D$_2$O/H$_2$O solvent, and the ^{7}Li resonance of this solution was used as an external reference. Bulk diamagnetic susceptibility corrections of the ^{7}Li chemical shifts were made by using the expression

$$\delta_{cor} = \delta_{obs} - 4\pi/3(\chi_{ref} - \chi) \qquad (1)$$

where δ_{cor} and δ_{obs} are the corrected and observed chemical shifts and χ_{ref} and χ are the volume diamagnetic susceptibilities of the reference and sample solutions, respectively.[19] A Johnson Matthey magnetic susceptibility balance was used to determine χ_{ref} and χ.

^{7}Li NMR spectra were run on a Bruker CXP-300 spectrometer operating at 116.59 MHz. For each solution an average of 6000 transients was accumulated in a 2048-point data base, and in the variable-temperature studies data were collected at temperature intervals of ca. 5 K. Sample temperature was controlled by a Bruker B-VT1000 variable-temperature unit to within ±0.3 K. To derive kinetic data, the Fourier-transformed spectra were subjected to complete line-shape analysis[20] on a Nicolet BNC12 minicomputer. The ^{7}Li line widths and chemical shifts (and their temperature dependences) employed in the line-shape analysis were obtained through a combination of extrapolation from low temperatures, where no exchange-induced modification occurred, and the determination of ^{7}Li line widths and shifts in solutions containing either solvated Li$^+$ or [Li.C21C$_5$]$^+$ alone in the coalescence temperature range observed for the solutions that contained both species.

Stability constants for [Ag.C21C$_5$]$^+$ were determined by the potentiometric titration of 25 cm^3 of 10^{-3} mol dm^{-3} AgClO$_4$ solution with 10^{-2} mol dm^{-3} C21C$_5$ solution. These data were employed in the derivation of the stability constants of [Li.C21C$_5$]$^+$ from data obtained from a competitive potentiometric titration of 25 cm^3 of 10^{-3} mol dm^{-3} AgClO$_4$ solution with a solution 10^{-2} mol dm^{-3} in both LiClO$_4$ and C21C$_5$ as described in the literature.[21] All solutions were 0.05 mol dm^{-3} in Et$_4$NClO$_4$. The titrations were carried out under dry nitrogen in a

---

(4) Cahen, Y. M.; Dye, J. L.; Popov, A. I. *J. Phys. Chem.* **1975**, *79*, 1289–1291.
(5) Cahen, Y. M.; Dye, J. L.; Popov, A. I. *J. Phys. Chem.* **1975**, *79*, 1292–1295.
(6) Popov, A. I. *Pure Appl. Chem.* **1979**, *51*, 101–110.
(7) Cox, B. G.; Garcia-Rosa, J.; Schneider, H. *J. Am. Chem. Soc.* **1981**, *103*, 1054–1059.
(8) Cox, B. G.; Garcia-Rosa, J.; Schneider, H. *J. Am. Chem. Soc.* **1981**, *103*, 1384–1389.
(9) Schmidt, E.; Tremillon, J.-M.; Kintzinger, J.-P.; Popov, A. I. *J. Am. Chem. Soc.* **1983**, *105*, 7563–7566.
(10) Lincoln, S. F.; Brereton, I. M.; Spotswood, T. M. *J. Chem. Soc., Faraday Trans. I* **1985**, *81*, 1623–1630.
(11) Lincoln, S. F.; Horn, E.; Snow, M. R.; Hambley, T. W.; Brereton, I. M.; Spotswood, T. M. *J. Chem. Soc., Dalton Trans.* **1986**, 1075–1080.
(12) Lincoln, S. F.; Steel, B. J.; brereton, I. M.; Spotswood, T. M. *Polyhedron* **1986**, *5*, 1597–1600.
(13) Lincoln, S. F.; Brereton, I. M.; Spotswood, T. M. *J. Am. Chem. Soc.* **1986**, *108*, 8134–8138.
(14) Clarke, P.; Abou-Hamdan, A.; Hounslow, A. M.; Lincoln, S. F. *Inorg. Chim. Acta* **1988**, *154*, 83–87.
(15) Abou-Hamdan, A.; Hambley, T. W.; Houslow, A. M.; Lincoln, S. F. *J. Chem. Soc., Dalton Trans.* **1987**, 489–492.
(16) Moras, D.; Weiss, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 400–403.
(17) Abou-Hamdan, A.; Brereton, I. M.; Hounslow, A. M.; Lincoln, S. F.; Spotswood, T. M. *J. Inclusion Phenom.* **1987**, *5*, 137–141.
(18) Perrin, D. D.; Aramaego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: Oxford, U.K., 1980.
(19) Live, D. H.; Chan, S. I. *Anal. Chem.* **1970**, *42*, 791–792.
(20) Lincoln, S. F. *Prog. React. Kinet.* **1977**, *9*, 1–91.
(21) Cox, B. G.; Schneider, H.; Stroka, J. *J. Am. Chem. Soc.* **1978**, *100*, 4746–4749.

Table II. Stability Constants for Cryptates of Monovalent Metal Ions Formed with the Cryptands 4,7,13-Trioxa-1,10-diazabicyclo[8.5.5]eicosane ($C21C_5$) and 4,7,13,18-Tetraoxa-1,10-diazabicyclo[8.5.5]eicosane (C211) in a Range of Solvents

	log (K/dm^3 mol^{-1}) (298.2 K)					
solvent	$[Ag.C21C_5]^+$	$[Ag.C211]^+$	$[Li.C21C_5]^+$	$[Li.C211]^+$	$[Na.C21C_5]^+$	$[Na.C211]^+$
acetonitrile	4.29[a,b] (4.55)[e]	7.70[c]	4.15[a,b]	>10[c]	5.08[e]	>9[c]
methanol	7.69[a,b] (7.62)[e]	10.61[f]	3.00[a,d]	8.04[f]	3.76[e]	6.7[g]
dimethylformamide	5.23[a,b] (5.19)[f]	8.62[c]	1.80[a,d,h]	6.99[c]	2.87[e]	5.23[c]
dimethylacetamide	4.45[a,d]		1.85[a,b]		2.05[e]	
diethylformamide	4.95[a,b]		1.72[a,b]		2.52[e]	

[a] This study (0.05 mol dm^{-3} Et_4NClO_4 supporting electrolyte). [b] Error is ±0.10 log unit. [c] Reference 8. [d] Error is ±0.15 log unit. [e] Reference 12 (0.05 mol dm^{-3} Et_4NClO_4 supporting electrolyte). [f] Reference 21 (0.10 and 0.05 mol dm^{-3} Et_4NClO_4 supporting electrolyte for $[Ag.C211]^+$ and $[Li.C211]^+$, respectively). [g] Lejaille, M.-F.; Livertoux, M.-H.; Guidon, C.; Bessiere, J. *Bull. Soc. Chim. Fr.* **1978**, *19*, 1373–1377 (0.10 mol dm^{-3} Bu_4NClO_4 supporting electrolyte). [h] This value is revised from the preliminary value quoted in ref 15.

thermostated (298.2 ± 0.01 K) titration vessel connected to a thermostated reference vessel by a salt bridge containing a 0.05 mol dm^{-3} Et_4NClO_4 solution. The reference and titration electrodes were silver; the reference solution was 10^{-2} mol dm^{-3} $AgClO_4$ in the solvent under investigation. An Orion Research SA 720 Digital analyzer was used to measure changes in potential.

Results and Discussion

Cryptate Structure in Solution. In the solid state, both $[Li.C211]^+$ and $[Li.C21C_5]^+$ exist as inclusive cryptates in which Li^+ resides inside the cryptand cavity. In both cryptates, the cryptands exist in the endo–endo conformation in which both nitrogen lone electron pairs point toward the center of the cryptand cavity. Thus in $[Li.C211]^+$ the Li^+ is at the focus of six lone electron pairs directed toward the cavity center, and in $[Li.C21C_5]^+$ the Li^+ is at the focus of five such electron pairs. If these structures are retained in solution and the complexed Li^+ does not interact with the solvent, the ^7Li chemical shift of the cryptates should be independent of the nature of the solvent, in contrast to the chemical shift of the solvated Li^+ ion, which directly reflects the influence of the solvent on the magnetic field seen at the ^7Li nucleus.[4]

In a range of solvents the ^7Li chemical shift of $[Li.C211]^+$ is substantially independent of the nature of the solvent, indicating that the interaction of the complexed Li^+ with solvent is minimal as anticipated for an inclusive cryptate.[4] In contrast, the ^7Li chemical shifts of $[Li.C21C_5]^+$, δ_{cor}, vary over a 1.83 ppm range for the solvents studied, which compares with a range of 2.62 ppm for solvated Li^+ (Table I). This suggests that direct interaction between Li^+ in $[Li.C21C_5]^+$ and solvent occurs despite the inclusive structure observed for this cryptate in the solid state.[15] It is seen from the space-filling representation[22] of inclusive $[Li.C21C_5]^+$ (Figure 1) that Li^+ is not exposed at the exterior surface of the cryptate and that interaction with solvent can only occur if Li^+ moves from the center of the cryptand cavity toward the 15-membered diazatrioxa ring (this ring is chosen, as it contains five donor groups as opposed to four in the 15-membered diazadioxa ring) to produce an exclusive structure for $[Li.C21C_5]^+$. As there is no electron-donating group in the $-(CH_2)_5-$ moiety of $C21C_5$, there is unlikely to be substantial hindrance to this movement, which allows Li^+ to increase its coordination number to 6 or more through interaction with solvent. Thus a minimum of two equilibra are required to describe the complexation of Li^+ by $C21C_5$ (Figure 2), where the equilibrium between exclusive and inclusive $[Li.C21C_5]^+$ moves increasingly toward the exclusive cryptate as the ability of the solvent to coordinate Li^+ increases. The Gutmann donor number, D_N,[23,24] reflects the solvent coordinating ability, and it is seen from Table I that for the oxygen donor solvents δ_{cor} for $[Li.C21C_5]^+$ tends to increase with increase in D_N. The nitrogen donor solvents produce very different δ_{cor} values for $[Li.C21C_5]^+$. Unfortunately, the exclusive/inclusive equilibria characterizing $[Li.C21C_5]^+$ cannot be quantified, as the δ_{cor} data do not permit the determination of the specific chemical shifts of exclusive and inclusive $[Li.C21C_5]^+$ required to calculate equilibrium constants. (The ^{39}K chemical shift of inclusive $[K.C222]^+$ is also solvent independent while that of exclusive $[K.C221]^+$ is solvent dependent, and an equilibrium between exclusive and inclusive forms of $[Cs.C222.]^+$ has been reported.[25,26])

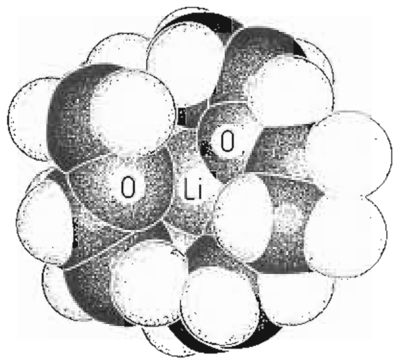


Figure 1. Structure of *inclusive* $[Li.C21C_5]^+$ viewed from above the 15-membered diazatrioxa ring. The $-(CH_2)_2O(CH_2)_2O(CH_2)_2-$ arm is to the right, and the first O is clearly seen, but only a small segment of the second O is visible adjacent to the H below the first O. The $-(CH_2)_2O(CH_2)_2-$ arm is to the left, and its O is clearly visible. Small segments of each N (shown in lighter shading than the adjacent C) are seen at the top and bottom of Li. The atomc coordinates are taken from the crystal structure,[15] and all atoms are shown as spheres of appropriate radii. The structural diagram was generated by using the program SCHAKAL.[22]

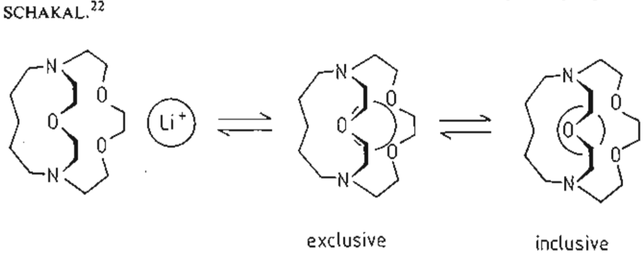


Figure 2. Representation of the two major equilibria in the $[Li.C21C_5]^+$ system.

Cryptate Stability Constants. The relative stabilities of cryptates depend on the electrostatic interactions between metal ions and cryptands, the solvation energies of metal ions and cryptands, and the fit of the metal ion into the cryptand cavity. From the data presented in Table II, it is seen that the stability constants for $[M.C211]^+$ are substantially greater than those for $[M.C21C_5]^+$, consistent with the presence of the extra oxygen donor atom in

---

(22) Keller, E. SCHAKAL. Institut fur Anorganische Chemie der Universitat Freiburg, Freiburg, FGR.

(23) Gutmann, V. *Coordination Chemistry in Nonaqueous Solutions*; Springer-Verlag: Vienna, 1968.

(24) Erlich, R. H.; Roach, E.; Popov, A. I. *J. Am. Chem. Soc.* **1970**, *92*, 4989–4990.

(25) Shih, J.-S.; Popov, A. I. *Inorg. Chem.* **1980**, *19*, 1689–1692.

(26) Mei, E.; Popov, A. I.; Dye, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 6532–6536.

Table III. Solution Composition and Kinetic Parameters for Lithium Ion Exchange on ($[Li.C21C_5]^+$) in Methanol, Dimethylformamide, Diethylformamide, and Dimethylacetamide

soln	solvent	$[Li^+(\text{solvated})]$, mol dm^{-3}	$[Li.C21C_5^+]$, mol dm^{-3}	k_d(298.2 K), s^{-1}	ΔH_d^*, kJ mol^{-1}	ΔS_d^*, J K^{-1} mol^{-1}
i	methanol	0.0530	0.0420	20.4 ± 0.4	37.2 ± 0.8	−95.0 ± 2.8
ii	methanol	0.0360	0.0590	22.7 ± 0.5	34.9 ± 0.9	−101.6 ± 3.3
i–ii	methanol			21.6 ± 0.4	36.1 ± 0.9	−98.4 ± 3.1
iii	dimethylformamide	0.0150	0.0074	120 ± 3	38.9 ± 1.3	−74.8 ± 4.7
iv	dimethylformamide	0.0120	0.0079	110 ± 5	38.0 ± 2.3	−77.5 ± 3.4
v	dimethylformamide	0.0110	0.0110	120 ± 3	34.0 ± 1.1	−73.1 ± 4.3
vi	dimethylformamide	0.0058	0.0140	120 ± 3	39.3 ± 1.0	−78.7 ± 3.6
iii–vi	dimethylformamide			116 ± 2	38.4 ± 0.9	−76.5 ± 3.0
vii	diethylformamide	0.0170	0.0091	215 ± 5	27.7 ± 1.6	−110.3 ± 5.3
viii	diethylformamide	0.0091	0.0170	196 ± 3	29.0 ± 1.2	−103.5 ± 4.2
vii–viii	diethylformamide			210 ± 4	27.8 ± 1.5	−107.6 ± 5.3
ix	dimethylacetamide	0.0140	0.0071	241 ± 6	49.0 ± 1.3	−34.0 ± 4.3
x	dimethylacetamide	0.0084	0.0126	235 ± 5	48.9 ± 1.1	−35.6 ± 3.8
ix–x	dimethylacetamide			237 ± 4	49.0 ± 2.1	−35.0 ± 2.8

C211 generating a greater stability in its cryptates when $M^+ = Ag^+$, Li^+, and Na^+. This is probably a consequence of the greater electrostatic attraction of C211 for metal ions by comparison with $C21C_5$. In the common solvents studied, the relative stabilities $[Li.C211]^+ > [Na.C211]^+$ indicate that the optimum fit of Li^+ into the C211 cavity to produce an inclusive cryptate confers an increased stability over that of exclusive $[Na.C211]^+$, while the relative stabilities $[Li.C21C_5]^+ < [Na.C21C_5]^+$ suggest that $[Li.C21C_5]^+$ has lost this stabilizing feature. This is consistent with the variation of the ^7Li shift of $[Li.C21C_5]^+$ with solvent, which suggests that this cryptate exists substantially in the exclusive form, as does $[Na.C21C_5]^+$. In the oxygen donor solvents both Ag^+ (r = 115 pm) cryptates are considerably more stable than their Li^+ (r = 76 pm) and Na^+ (r = 102 pm) analogues, despite the larger ionic radius[27] (r) of Ag^+ rendering it a poorer fit for the cryptand cavities. This suggests that there is a difference in the interaction between the cryptands and nondirectional bonding Li^+ and Na^+ and directional bonding Ag^+, which has a tendency to form two strong coaxial bonds.[28] In acetonitrile $[Ag.C211]^+$ is less stable than its Li^+ and Na^+ analogues, and $[Ag.C21C_5]^+$ is of similar stability to its Li^+ analogue and less stable than its Na^+ analogue. This change probably reflects the tendency of Ag^+ to bond less effectively with oxygen donor atoms than with nitrogen donor atoms, with the consequence that a nitrogen donor solvent can compete more effectively with a cryptand for Ag^+ than can an oxygen donor solvent.[12,28]

Cryptate Metal Ion Exchange Kinetics. In acetonitrile, propylene carbonate, and acetone, the rate of exchange of Li^+ between the solvated and $[Li.C21C_5]^+$ environments is too slow to cause any significant broadening of the separate ^7Li resonances characterizing these environments up to the solvent boiling point temperature. However, in methanol, dimethylformamide, diethylformamide, and dimethylacetamide, a temperature-dependent coalescence of the ^7Li resonances arising from solvated Li^+ and $[Li.C21C_5]^+$ (Figure 3) yields the kinetic parameters for the decomplexation of $[Li.C21C5]^+$ (eq 2) shown in Table III. These

$$Li^+ + C21C_5 \underset{k_d}{\overset{k_c}{\rightleftharpoons}} [Li.C21C_5]^+ \qquad (2)$$

$$k_d = 1/\tau_c = (k_BT/h)\exp(-\Delta H_d^*/RT + \Delta S_d^*/R) \qquad (3)$$

parameters are derived from the temperature variation of the mean lifetime of $[Li.C21C_5]^+$, τ_c, through eq 3, in which all symbols have their usual meaning. The τ_c values ($\tau_c/X_c = \tau_s/X_s$, where τ is a lifetime, X is a mole fraction, and the subscripts c and s refer to Li^+ in the cryptate and solvated states, respectively) are derived through complete line-shape analysis[19] of the coalescing ^7Li resonances observed for solutions i–x (Table III), as exemplified by Figure 3.

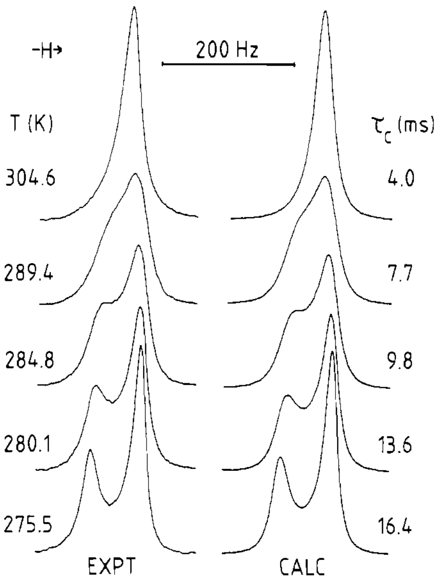


Figure 3. Typical exchange-modified 116.59-MHz ^7Li NMR spectra of a diethylformamide solution of $LiClO_4$ (0.0261 mol dm^{-3}) and $C21C_5$ (0.0170 mol dm^{-3}). Experimental temperatures and spectra appear to the left of the figure, and the best fit calculated line shapes and corresponding τ_c values appear to the right. The resonance of $[Li.C21C_5]^+$ appears upfield from that of solvated Li^+.

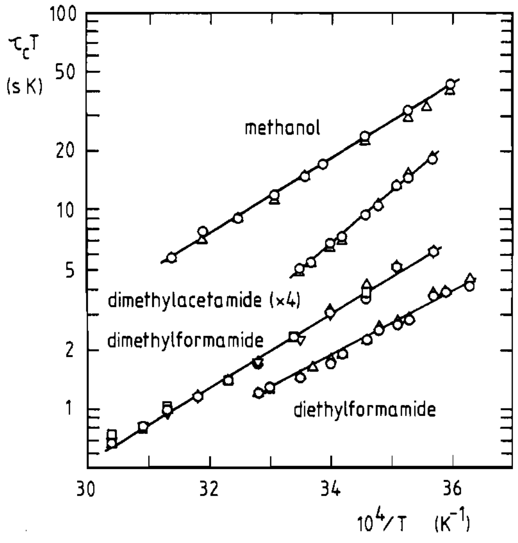


Figure 4. Temperature variation of τ_c for Li^+ exchange on $[Li.C21C_5]^+$. Data points for methanol solutions i and iii–vi are represented by circles and triangles, respectively, those for dimethylacetamide solutions ix and x by triangles and circles, respectively (these values are multiplied by 4), those for dimethylformamide solutions iii–vi by triangles, squares, circles, and inverted triangles, respectively, and those for diethylformamide solutions vii and viii by circles and triangles, respectively.

---

(27) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys. Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751–767.

(28) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd ed.; Interscience: New York, 1980.

Table IV. Kinetic Parameters[a] for Li^+ and Na^+ Exchange on Cryptates in a Range of Solvents

solvent	D_N[b]	$10^{-5}k_c$(298.2 K), $dm^3\ mol^{-1}\ s^{-1}$	k_d(298.2 K), s^{-1}	ΔH_d^*, kJ mol^{-1}	ΔS_d^*, J K^{-1} mol^{-1}
			$[Li.C21C_5]^+$		
acetonitrile	14.1	...	slow		
propylene carbonate	15.1	...	slow		
acetone	17.0	...	slow		
methanol	19.0 (23.5)[d]	0.221	21.6 ± 0.4	36.1 ± 0.9	−98.4 ± 3.1
dimethylformamide	26.6	0.073	116 ± 2	38.4 ± 0.9	−76.5 ± 3.0
diethylformamide	30.9	0.149	210 ± 4	27.8 ± 1.5	−108 ± 5
dimethylacetamide	27.8	0.124	237 ± 4	49.0 ± 2.1	−35.0 ± 2.8
			$[Li.C211]^+$		
dimethylformamide[e]	26.6	1.27	0.0130 ± 0.0033	64.4 ± 2.5	−64.8 ± 5.9
			$[Na.C21C_5]^+$		
acetonitrile[f]	14.1	100	84.8 ± 1.6	57.9 ± 0.7	−13.8 ± 2.1
propylene carbonate[f]	15.1	25.5	19.4 ± 0.5	70.3 ± 0.5	15.3 ± 1.4
acetone[f]	17.0	84	878 ± 6	54.4 ± 0.4	−6.1 ± 1.2
methanol[f]	19.0 (23.5)[d]	104	1800 ± 50	44.9 ± 0.1	−31.9 ± 0.4
dimethylformamide[f]	26.6	214	28 800 ± 300	40.0 ± 0.1	−25.3 ± 0.5
diethylformamide[g]	30.9	fast	fast		
dimethylacetamide[g]	27.8	fast	fast		
			$[Na.C211]^+$		
propylene carbonate[h]	15.1	210	0.036		
methanol[h]	19.0 (23.5)[d]	31.0	2.5		
dimethylformamide[i]	26.6	19.2	12.1 ± 0.2	83.5 ± 0.5	55.8 ± 1.2

[a] Quoted errors represent one standard deviation obtained from a linear regression analysis of the temperature dependence of experimental τ_c data through eq 3. [b] Gutmann donor number from ref 23. Dielectric constants from the same reference: acetonitrile, 38.0; propylene carbonate, 69.0; acetone, 20.7; methanol, 32.6; dimethylformamide, 36.1. [c] $k_c = k_dK$. [d] This alternative value of D_N has been suggested for methanol solution by: DeWitte, W. J.; Popov, A. I. *J. Soln. Chem.* **1976**, *5*, 231–240. [e] Reference 5. [f] Reference 13. [g] Reference 14. [h] Reference 8. [i] Reference 10.

It is seen from Figure 4 that the temperature variations of τ_c for each of the solutions studied for a given solvent are indistinguishable. Thus the mean lifetime of $[Li.C21C_5]^+$, τ_c $(=1/k_d)$, is independent of the concentration of solvated Li^+ (Table III), consistent with the nonparticipation of solvated Li^+ in the rate-determining step of the predominant pathway for Li^+ exchange on $[Li.C21C_5]^+$ and the operation of a monomolecular mechanism for the decomplexation of Li^+ from the cryptand. Monomolecular decomplexation mechanisms also operate for $[Li.C211]^+$, $[Na.C211]^+$, and $[Na.C21C_5]^+$.[5,10,13] However, it is not invariably the case that the monomolecular mechanism operates in cryptate systems. This is exemplified by $[Li.C221]^+$, for which the Li^+-exchange process changes from a monomolecular mechanism to a bimolecular mechanism (in which both the leaving and entering Li^+ ions are bound by C221 in the transition state) as the solvent dielectric constant increases.[29]

Variation in the nature of the solvent has a substantial effect on the magnitude of k_d characterizing $[Li.C21C_5]^+$. Of the four solvents for which quantitative data are available, the weaker electron-donating solvent, methanol, yields the smaller k_d value, while dimethylformamide, diethylformamide, and dimethylacetamide, which are of similar structure and D_N, yield k_d values grouped within a factor of 2 of each other over the experimental temperature range. (Nevertheless, this similarity of k_d is a consequence of differing, but compensating, ΔH_d^* and ΔS_d^* contributions for the last three solvents.) The k_c values exhibit a smaller variation than k_d, consistent with the variation of K for $[Li.C21C_5]^+$ in these solvents being predominantly determined by k_d variations, as is also observed for $[Na.C21C_5]^+$ and other cryptates (Table IV).

In dimethylformamide the greater stability of $[Li.C211]^+$, by comparison with $[Li.C21C_5]^+$, is predominantly a consequence of its 9000-fold smaller k_d, with a modest contribution arising from its 17-fold greater k_c. The smaller k_d for $[Li.C211]^+$ is attributable to the greater electrostatic interaction between Li^+ and the six donor atoms of C211, and the inclusive nature of the cryptate. In contrast, $C21C_5$ has five donor atoms and $[Li.C21C_5]^+$ exists, in part at least, in the exclusive form and is consequently expected to be more labile. The increase of k_d in the sequence $[Li.C211]^+ < [Na.C211]^+ < [Li.C21C_5]^+ < [Na.C21C_5]^+$ in dimethylformamide (Table IV) suggests that the greater electrostatic attraction of C211 for Li^+ and Na^+ is a particularly important factor determining the decomplexation rate.

The greater stability of $[Na.C21C_5]^+$, by comparison to that of $[Li.C21C_5]^+$, in dimethylformamide is a consequence of the first cryptate possessing a 250-fold greater k_d and a 2900-fold greater k_c (Table IV). A similar relationship exists for methanol. The lower lability of $[Li.C21C_5]^+$ by comparison with $[Na.C21C_5]^+$ may be attributable to the smaller size of Li^+ and its consequently stronger electrostatic interaction with ligands. Thus the magnitude of k_c partially reflects the sequential desolvation of Li^+, which is more strongly solvated than Na^+, and, in consequence, k_c for $[Li.C21C_5]^+$ is significantly smaller than that for $[Na.C21C_5]^+$. Similarly, the smaller value of k_d for $[Li.C1C_5]^+$ probably reflects the greater electrostatic interaction between Li^+ and $C21C_5$.

The tendency for k_d characterizing $[LiC21C_5]^+$ and $[Na.C21C_5]^+$ to increase as solvent D_N increases (Table IV) indicates that the influence of the solvent is similar for both cryptates. [There is no apparent correlation between the solvent dielectric constant and k_d (Table IV).] The decomplexation mechanism involves sequential resolvation of the metal ion and accompanying stereochemical changes. However, the gross aspects of the variation of k_d may be explained on the basis of eq 4, where ΔG_d^*

$$\Delta G_d^* = \Delta G_r^* - \Delta G_s^* \qquad (4)$$

for decomplexation is the difference between ΔG_r^*, the free energy change arising from structural rearrangements in $[M.C21C_5]^+$ to reach its transition state stereochemistry in the absence of solvent, and ΔG_s^*, the free energy change arising from involvement of solvent in the activation process, which causes an increase of M^+ solvation in $[M.C21C_5]^+$ in the transition state. As ΔG_r^* is defined to be independent of solvent, it is evident that as ΔG_s^* increases with the D_N of the solvent, ΔG_d^* decreases and k_d increases.[13] Similar increases in k_d and solvent D_N have been observed for other cryptates.[6,10]

---

(29) Shamsipur, M.; Popov, A. I. *J. Phys. Chem.* **1986**, *90*, 5997–5999.

Conclusion

The variation of the ^7Li chemical shift of $[Li.C21C_5]^+$ with the nature of the solvent is consistent with significant proportions of this cryptate being in the exclusive form in solution despite its existence in the inclusive form in the solid state. The stability constants characterizing $[Li.C21C_5]^+$ are smaller than those of $[Na.C21C_5]^+$, which is also consistent with the former cryptate existing substantially in the exclusive form. The exchange of Li^+ on $[Li.C21C_5]^+$ proceeds through a monomolecular mechanism, and the decomplexation rate constant, k_d, increases with solvent D_N, consistent with increasingly strong solvation of the transition state producing decreases in ΔG_d^* for decomplexation.

Acknowledgment. We thank A. H. Hounslow for her assistance in the NMR measurements and the University of Adelaide for supporting this research. The award of a Commonwealth Postgraduate Award to A.A.-H. is gratefully acknowledged.

Contribution from the Department of Chemistry,
The Florida State University, Tallahassee, Florida 32306

Complexation of the Uranyl Ion (UO_2^{2+}) with Phenylene-1,2-dioxydiacetic Acid

L. F. Rao[†] and G. R. Choppin*

Received February 12, 1990

Complexation of uranyl cations by phenylene-1,2-dioxydiacetic acid has been studied by potentiometry, calorimetry, solvent extraction, and ^1H NMR spectroscopy. Complexation parameters at 298 K and 0.1 M ($NaClO_4$) ionic strength are as follows: $\log \beta_{101} = 3.01 \pm 0.05$; $\log \beta_{111} = 5.22 \pm 0.04$; $\Delta H_{101} = 16.8 \pm 0.2$ kJ mol^{-1}; $\Delta S_{101} = 114 \pm 5$ J K^{-1} mol^{-1}; $\Delta H_{111} = 10.4 \pm 0.5$ kJ mol^{-1}; $\Delta S_{111} = 68 \pm 5$ J K^{-1} mol^{-1}. The thermodynamic and NMR data are consistent with bonding of UO_2^{2+} to the carboxylate groups of the ligand, with weak or no interaction with the ether oxygens. No 1:2 complexation was observed.

Introduction

Earlier studies[1,2] from this laboratory of the complexation of trivalent lanthanides by phenylene-1,2-dioxydiacetic acid showed that the ether oxygens are involved in the tetradentate chelation. The nuclear magnetic resonance study[2] of the complexes in solution provided evidence for strong bonding of the ether oxygens to the lanthanide ions in the 1:1 complex but weaker bonding and longer metal–ether oxygen distances in the 1:2 complex. In the present work potentiometry, solvent extraction, nuclear magnetic resonance spectroscopy, and calorimetry have been employed to study the complexation between the uranyl cation (UO_2^{2+}) and phenylene-1,2-dioxydiacetic acid. The data on uranyl complexation are compared to those on lanthanide complexation to clarify the effects of cationic charge and of the steric interactions imposed by the linear structure of the uranyl cation.

Experimental Section

Reagents. Phenylene-1,2-dioxydiacetic acid (PDOA), from Aldrich Chemical Co., was recrystallized twice from water. For the potentiometric titrations and the solvent extraction experiments, a stock solution of 0.02 M was prepared by dissolving the purified compound in 0.01 M NaOH. The pH of the stock solution ranged from 2.5 to 3.5. Working solutions were made by dilution of the stock solution with appropriate amounts of $NaClO_4$ solution to obtain an ionic strength of 0.10 M. For the nuclear magnetic resonance experiments, all solutions were prepared in D_2O and the stock solution of PDOA was prepared by dissolving it in NaOD.

The stock solution of uranyl perchlorate was prepared from reagent grade $UO_2(ClO_4)_2(H_2O)_6$ (Aldrich Chemical Co.) and was standardized by spectrophotometry.[3] In the solvent extraction experiments, the stock solution of ^{233}U tracer was prepared from high-purity $^{233}UO_2$ (Oak Ridge National Laboratory) by dissolution in fuming HNO_3, evaporation to dryness, and redissolution in $HClO_4$.

The extracting agent was dinonylnaphthalenesulfonic acid, HDNNS, from R. T. Vanderbilt Co., and was used without further purification. The stock solution of HDNNS was standardized by following the procedures described in an early work.[4] The heptane solutions used for extraction study were prepared at the desired concentrations by dilution of the stock solution.

Ecolume (ICN Radiochemicals) was used as the scintillation solution for counting the α-radioactivity of ^{233}U on a Packard Tri-Carb 4000 Series liquid scintillation counter.

Procedures. Potentiometric titrations were performed in a glass vessel jacketed to allow a flow of water from a water bath to maintain the temperature at 25.0 ± 0.1 °C. The hydrogen ion concentration was measured with a Corning 130 pH meter equipped with a Corning combination electrode.

Solvent extraction was carried out by using the methods described in previous publications.[5] Aqueous solutions (5 mL) of PDOA, in concentrations ≤0.02 M, plus $^{233}UO_2^{2+}$, at tracer concentrations, were equilibrated with equal volumes of heptane solutions of HDNNS. After overnight equilibration at 25.0 °C in a water bath, the phases were separated. Aliquots of 1.00 mL were taken from each phase and mixed with 5 mL of Ecolume for counting the radioactivity.

The NMR measurements were performed on the Bruker 270-MHz spectrometer of the FSU NMR Laboratory on samples prepared by mixing weighed amounts of uranyl perchlorate and PDOA/D_2O solutions. The pD of these samples was adjusted with NaOD solution to about 4.2. Sodium 2,2-dimethyl-2-silapentanesulfonate (DSS) was used as an internal standard.

Calorimetric titrations were performed by using a calorimeter and by techniques that have been described previously.[6] The titration was duplicated in a beaker outside the calorimeter to measure the pH values after each addition of titrant. The titrations were done with the $UO_2(ClO_4)_2$ solution (ca. 5 mM) in the calorimeter cup and with the ligand buffer solution (ca. 12 mM) as the titrant. The corrections for the heats of dilution of the metal and the ligand were determined in separate runs. Values of the enthalpies of protonation for the PDOA ligand from ref 2 were used in the calculations.

Data Analysis. The proton dissociation constants of PDOA were calculated from the potentiometric titration data by least-squares methods using the equation

$$\frac{\bar{n}_H}{(1-\bar{n}_H)[H^+]} = \frac{1}{K_{a2}} + \frac{1}{K_{a1}K_{a2}}\frac{(2-\bar{n}_H)[H^+]}{1-\bar{n}_H} \qquad (1)$$

where $\bar{n}_H$ is the average number of ionizable hydrogen atoms bound per ligand anion and K_{a1} and K_{a2} are the first and second acid dissociation constants, respectively.

The linear least-squares method was used for calculation of the stability constants of the metal complexes (β_{101} for ML and β_{102} for ML_2) from the potentiometric titration data according to the equation[7]

$$\frac{\bar{n}}{(1-\bar{n})[L]} = \beta_{101} + \frac{(2-\bar{n})}{1-\bar{n}}\beta_{102}[L] \qquad (2)$$

[†] On leave from the Institute of Atomic Energy, Beijing, China.

(1) Hasegawa, Y.; Choppin, G. R. *Inorg. Chem.* **1977**, *16*, 2931.
(2) Kullberg, L.; Choppin, G. R. *Inorg. Chem.* **1977**, *16*, 2926.
(3) Rabinowitch, E.; Belford, R. L. *Spectroscopy and Photochemistry of Uranyl Compounds*; Macmillan: New York, 1964.
(4) White, J. M. *J. Inorg. Nucl. Chem.* **1960**, *14*, 255.
(5) Choppin, G. R.; Unrein, P. J. In *Transuranium Elements*; Muller, W., Lindner, R. Eds.; North Holland: Amsterdam, 1976; p 97.
(6) Caceci, M. S.; Choppin, G. R. *Comput. Chem.* **1982**, *6*, 161.

0020-1669/90/1329-3589$02.50/0