A Structural Study of the Complexation of the Lithium Ion by the Cryptand 4,7,13-Trioxa-1,10-diazabicyclo[8.5.5]icosane†

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The crystal structure of the cryptate [LiL^3]NCS, formed with the cryptand 4,7,13-trioxa-1,10-diazabicyclo[8.5.5]icosane (L^3) has been determined by single-crystal *X*-ray diffraction techniques at 294 K and refined by least-squares methods to a conventional *R* value of 0.068 for 1 101 reflections. The crystal was of space group $P2_1/n$ with a = 8.348(2), b = 24.798(7), c = 9.161(2) Å, β = 90.74(2)°, and Z = 4. The cryptate exists in the inclusive form in which the lithium ion resides in the cavity of L^3 and is within bonding distances of the two nitrogens and the three oxygens of the cryptand. These bonding distances are in the range 2.00(2)—2.36(3) Å and the geometry about lithium is very irregular. The thiocyanate is not within bonding distance of lithium in [LiL^3]NCS, in contrast to [NaL^3(NCS)] which exists in the exclusive form and in which thiocyanate is within bonding distance of sodium. The kinetic and equilibrium aspects of [LiL^3]$^+$ and [NaL^3]$^+$, and their analogues with 4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]icosane in dimethylformamide solution are also discussed.

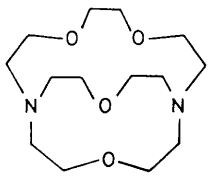
The polyoxadiazabicycloalkanes or cryptands[1] complex alkali-metal ions (M$^+$) to form inclusive cryptates in which M$^+$ is enclosed within the cryptand cavity and exclusive cryptates in which M$^+$ resides on the outside of a face of the cryptand. The inclusive cryptates are exemplified by [LiL^1]I[2] and [NaL^2]NCS[3] and the exclusive cryptates are exemplified by [NaL^1(NCS)],[4] [NaL^3(NCS)],[4] and [KL^2(NCS)][3] whose structures have been determined by single-crystal *X*-ray diffraction methods. N.m.r. studies[4—7] indicate that these inclusive and exclusive structures are largely retained in solution, and also that [LiL^3]$^+$ exists predominantly as an inclusive cryptate in solution. Such observations have major implications in the interpretation of the lability and stability variations of the alkali-metal ion cryptates.[7,‡]

As part of a wider investigation of cryptates and related species this *X*-ray diffraction study examines the structural effects of replacing an oxygen of L^1 by a methylene group to give 4,7,13-trioxa-1,10-diazabicyclo[8.5.5]icosane (L^3) on the complexation of Li$^+$ in the solid state. The effect of these changes on cryptate solution chemistry are also considered.

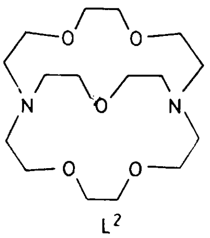
Experimental

Materials.—Lithium thiocyanate was dried at 353—363 K under high vacuum for 48 h and was stored over P_2O_5 under vacuum. The cryptand L^3 was prepared as previously described.[4] Crystals of [LiL^3]NCS were prepared by evaporating a methanolic solution equimolar in Li(NCS) and L^3 to a viscous oil on a vacuum line, redissolving in acetone, and equilibrating over several weeks with light petroleum (b.p. 40—60 °C) whereupon plate-like crystals were obtained.

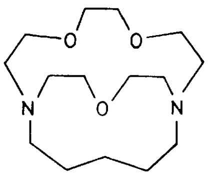
Crystallography.—*Crystal data.* $C_{16}H_{30}LiN_3O_3S$, M = 351.44, monoclinic, space group $P2_1/n$, a = 8.348(2), b = 24.798(7), c = 9.161(2) Å, β = 90.74(2)°, U = 1 896.2 Å^3, Z = 4, D_c = 1.231 g cm^{-3}, μ(Mo-K_α) = 1.49 cm^{-1}, λ(Mo-K_α) = 0.7107 Å, F(000) = 752.



L^1



L^2



L^3

Data collection. A plate-shaped crystal of dimensions 0.30 × 0.25 × 0.08 mm was mounted on a glass fibre with cyanoacrylate glue. Lattice parameters at 294 K were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured and refined by scans on an Enraf-Nonius CAD4 four-circle diffractometer employing graphite-monochromated Mo-K_α radiation. Intensity data were collected in the range $1 < \theta < 25°$ using an $\omega^{-4}/3$ scan. The scan width and horizontal apertures employed were (1.00 + 0.35 tanθ)° and (2.40 + 0.050 tanθ) mm respectively. Data reduction and application of Lorentz, polarisation, and decomposition corrections were performed using the program SUSCAD.[8] Of the 1 910 independent reflections collected 1 101 with $I > 2.5\sigma(I_o)$ were considered observed and used in the calculations.

Structure solution and refinement. The structure was solved by direct methods (MULTAN[9]) which revealed all non-hydrogen atoms except lithium. The thiocyanate ion is disordered over the two sites with an occupancy ratio of 80:20. Hydrogen atoms were included at calculated sites (C–H 0.97 Å). All non-hydrogen atoms were modelled with anisotropic thermal parameters while hydrogen atoms were assigned isotropic group thermal parameters. Block-matrix least-squares refinement of all positional and thermal parameters and an overall scale factor converged, all shifts < 1.0σ, with R = 0.068, R' = 0.073, and $w = 5.24/[\sigma^2(F_o) - 0.000\,09\ F_o^2]$.§ Maximum excursions in a final difference map were ±0.25 e Å^{-3}. Reflections with $k + 1$ odd were on average five times greater

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

‡ In ref. 7 the units of k_f should be dm^3 mol^{-1} s^{-1}.

§ $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma F_o^2]^{\frac{1}{2}}$.

than those with $k + 1$ even, reflecting an approximate two-fold axis through the structure at $\frac{1}{4},y,0$. The pseudo-symmetry complicated both the solution and the refinement of the structure, and presumably contributed to the relatively high final R index. Scattering factors and anomalous dispersion terms were taken from the literature.[10] All calculations were carried out using SHELX 76 [11] and ORTEP.[12]

The atom numbering scheme is given in the Figure. Final atomic co-ordinates, bond distances, and bond angles are given in Tables 1—3 respectively.

Results and Discussion

The structural analysis shows $[LiL^3]NCS$ to be an inclusive cryptate in which lithium resides within the L^3 cavity and is within bonding distance of the two nitrogens and the three oxygens of the cryptand. The thiocyanate anion is not within bonding distance of lithium and there are no contacts between it and the cryptate which are significantly less than the sum of the relevant van der Waals radii. This is in contrast to the exclusive cryptate $[NaL^3(NCS)]$ in which the thiocyanate nitrogen is within bonding distance of sodium.[4] The bond distances to lithium are within the range 2.00(2)—2.36(3) Å which compares with the ranges of 2.081(6)—2.288(7) and 2.151(6)—2.255(6) Å respectively observed for the inclusive cryptates $[LiL^1]^+$ and $[LiL^4]^+$ (L^4 = 4,7,13,16-tetraoxa-1,10-diazabicyclo[8.8.2]-icosane).[2,13]

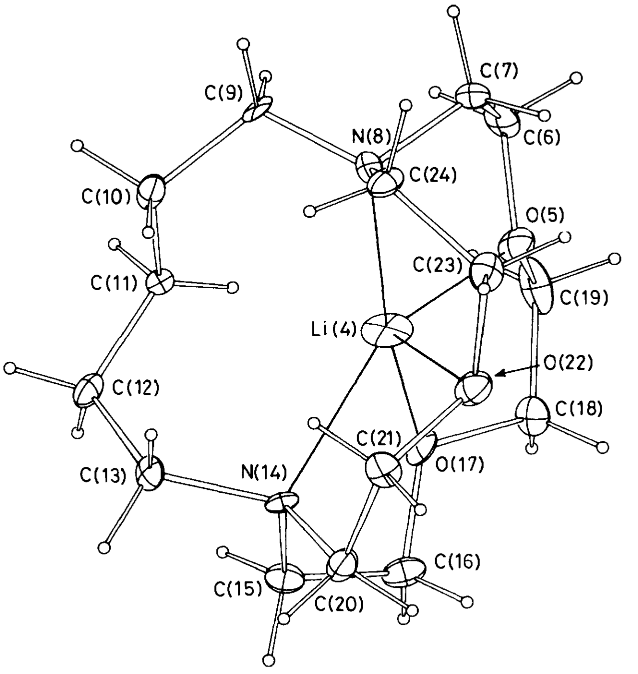

Figure. ORTEP plot of the structure of $[LiL^3]NCS$ showing the atomic numbering

The structural differences between $[LiL^3]NCS$ and $[NaL^3(NCS)]$ are a consequence of Na^+ being too large to be accommodated by the L^3 cavity, and a similar explanation holds for the structural differences between $[LiL^1]I$ and $[NaL^1(NCS)]$. (The effective six-co-ordinate ionic radii [14] of Li^+ and Na^+, and the internal diameters of the L^1 and L^3 cavities [1,15] are 0.76, 1.02, 1.6, and 1.6 Å respectively.) However, the fourth oxygen in L^1 provides an inducement for Li^+ to enter the cryptand cavity in $[LiL^1]^+$ which is absent in $[LiL^3]^+$. Thus the inclusive form of the latter cryptate is in part at least attributable to the *endo,endo* conformation of L^3 in the cryptate. This results in the lone electron pairs of both nitrogens being directed towards the centre of the cavity, and thereby providing a bonding interaction with Li^+ which is stronger than that anticipated if Li^+ remained outside the cavity.

In dimethylformamide (dmf) solution there are substantial differences in both the stability and the lability of the cryptates formed by L^1 and L^3. N.m.r. studies [7,16] of the M^+ (M = Li or Na) exchange process shown in equation (1), in which the

Table 2. Bond lengths (Å) for $[LiL^3]NCS$

C(2)–S(1)	1.717(29)	N(3)–C(2)	0.966(24)
O(5)–Li(4)	2.001(21)	N(8)–Li(4)	2.111(19)
C(11)···Li(4)	2.573(25)	N(14)–Li(4)	2.275(23)
O(17)–Li(4)	2.142(16)	O(22)–Li(4)	2.360(27)
C(6)–O(5)	1.407(12)	C(19)–O(5)	1.424(13)
C(7)–C(6)	1.557(16)	N(8)–C(7)	1.474(12)
C(9)–N(8)	1.438(9)	C(24)–N(8)	1.408(12)
C(10)–C(9)	1.488(11)	C(11)–C(10)	1.462(12)
C(12)–C(11)	1.463(12)	C(13)–C(12)	1.490(11)
N(14)–C(13)	1.548(11)	C(15)–N(14)	1.445(11)
C(20)–N(14)	1.548(10)	C(16)–C(15)	1.464(14)
O(17)–C(16)	1.426(10)	C(18)–O(17)	1.438(12)
C(19)–C(18)	1.453(14)	C(21)–C(20)	1.540(12)
O(22)–C(21)	1.478(11)	C(23)–O(22)	1.495(11)
C(24)–C(23)	1.534(12)		

Table 1. Atomic co-ordinates (× 10^4) for $[LiL^3]NCS$ *

Atom	x	y	z	Atom	x	y	z
S(1)	2 272(9)	4 150(1)	10 010(9)	C(12)	4 321(9)	3 295(4)	3 836(10)
S(1′)	3 043(93)	4 088(29)	9 603(50)	C(13)	5 764(10)	3 139(3)	2 994(10)
C(2)	2 435(29)	3 464(10)	9 797(20)	N(14)	6 949(7)	3 614(3)	2 822(6)
C(2′)	1 972(60)	3 514(20)	10 337(55)	C(15)	6 314(11)	4 023(4)	1 852(10)
N(3)	2 236(22)	3 086(5)	9 964(20)	C(16)	7 147(11)	4 536(5)	2 071(10)
N(3′)	2 669(62)	3 089(23)	10 558(64)	O(17)	6 947(7)	4 658(3)	3 579(7)
Li(4)	7 499(30)	4 002(6)	5 022(22)	C(18)	7 628(12)	5 157(4)	4 090(13)
O(5)	8 053(7)	4 658(3)	6 199(8)	C(19)	7 433(12)	5 156(5)	5 664(28)
C(6)	7 770(12)	4 566(5)	7 689(13)	C(20)	8 513(9)	3 368(4)	2 224(10)
C(7)	8 428(11)	3 989(5)	8 005(9)	C(21)	9 495(10)	3 116(4)	3 484(10)
N(8)	7 767(7)	3 577(3)	7 007(7)	O(22)	9 909(7)	3 538(3)	4 564(7)
C(9)	6 225(9)	3 409(4)	7 522(8)	C(23)	10 360(10)	3 307(4)	6 020(11)
C(10)	5 232(10)	3 145(4)	6 366(10)	C(24)	8 896(10)	3 156(4)	6 929(10)
C(11)	4 761(9)	3 535(4)	5 244(9)				

* The thiocyanate ion is disordered over two sites with an occupancy ratio of 80 : 20. The more populated site is occupied by atoms S(1), C(2), and N(3).

Table 3. Bond angles (°) for [LiL^3]NCS

N(3)–C(2)–S(1)	158.5(29)	N(8)–Li(4)–O(5)	85.5(9)
N(14)–Li(4)–O(5)	149.7(9)	N(14)–Li(4)–N(8)	124.7(8)
O(17)–Li(4)–O(5)	76.3(6)	O(17)–Li(4)–N(8)	158.5(13)
O(17)–Li(4)–N(14)	74.6(7)	O(22)–Li(4)–O(5)	107.5(11)
O(22)–Li(4)–N(8)	80.1(7)	O(22)–Li(4)–N(14)	78.4(8)
O(22)–Li(4)–O(17)	115.9(11)	C(6)–O(5)–Li(4)	110.5(8)
C(19)–O(5)–Li(4)	116.0(8)	C(19)–O(5)–C(6)	114.2(10)
C(7)–C(6)–O(5)	105.5(8)	N(8)–C(7)–C(6)	113.2(8)
C(7)–N(8)–Li(4)	102.8(8)	C(9)–N(8)–Li(4)	110.0(9)
C(9)–N(8)–C(7)	109.0(8)	C(24)–N(8)–Li(4)	112.9(9)
C(24)–N(8)–C(7)	107.4(7)	C(24)–N(8)–C(9)	113.9(8)
C(10)–C(9)–N(8)	112.7(7)	C(11)–C(10)–C(9)	110.6(8)
C(12)–C(11)–C(10)	114.4(9)	C(13)–C(12)–C(11)	111.5(7)
N(14)–C(13)–C(12)	112.1(7)	C(13)–N(14)–Li(4)	110.8(7)
C(15)–N(14)–Li(4)	108.4(7)	C(15)–N(14)–C(13)	111.5(7)
C(20)–N(14)–Li(4)	108.6(8)	C(20)–N(14)–C(13)	106.3(7)
C(20)–N(14)–C(15)	111.2(7)	C(16)–C(15)–N(14)	110.9(8)
O(17)–C(16)–C(15)	104.8(9)	C(16)–O(17)–Li(4)	114.3(9)
C(18)–O(17)–Li(4)	111.8(8)	C(18)–O(17)–C(16)	116.6(9)
C(19)–C(18)–O(17)	105.9(11)	C(18)–C(19)–O(5)	107.3(10)
C(21)–C(20)–N(14)	109.7(7)	O(22)–C(21)–C(20)	109.4(8)
C(21)–O(22)–Li(4)	105.7(7)	C(23)–O(22)–Li(4)	103.5(7)
C(23)–O(22)–C(21)	112.3(8)	C(24)–C(23)–O(22)	112.6(7)
C(23)–C(24)–N(8)	112.7(9)		

Table 4. Rate and apparent stability constants for cryptate systems in dmf solution at 298.2 K

M^+	Cryptand	k_d/s^{-1}	$10^{-5}k_f$/ dm^3 mol^{-1} s^{-1}	log (K/ dm^3 mol^{-1})	Ref.
Li^+	L^3	107	0.67	2.80	*a*
Li^+	L^1	0.013	1.27	6.99	16
Na^+	L^3	2.88×10^4	214	2.87	*b*
Na^+	L^1	12.1	19.2	5.20	7

[a] A. Abou-Hamdan, unpublished work. [b] Ref. 4, and I. M. Brereton, unpublished work.

cryptand (L) is either L^1 or L^3, yield the rate constants k_d and k_f

$$M^+ + L \underset{k_d}{\overset{k_f}{\rightleftharpoons}} [ML]^+ \qquad (1)$$

for these four systems in dmf shown in Table 4 which also contains the apparent stability constants K ($= k_f/k_d$). It is seen that, for a given cryptand, [LiL]$^+$ is less labile than [NaL]$^+$, and that for a given metal ion, [ML^1]$^+$ is more stable than [ML^3]$^+$ mainly as a consequence of the latter cryptate being characterised by a much larger k_d value.

In general cryptate dissociation is expected to proceed sequentially through a number of metal-ion resolvation and metal-ion to cryptand bond-breaking steps, but only those with the higher $\Delta G^‡$ values will be detected by kinetic techniques. As it appears that [NaL]$^{+}$* and [LiL]$^+$ exist in solution predominantly as the exclusive and inclusive cryptates respectively[4–7] it is likely that the smaller k_d values observed for [LiL]$^+$ are a consequence of the slowest of the sequential steps in the dissociation process involving a change from the exclusive to the inclusive form of the cryptate. The substantially greater k_d values observed for [ML^3]$^+$ compared to those observed for [ML^1]$^+$ indicate that the bonding interaction between either Li$^+$ or Na$^+$ and the fourth oxygen in L^1 makes a significant contribution to $\Delta G^‡$ characterising the slowest step in the dissociation of [ML^1]$^+$. This seems reasonable in the case of inclusive [LiL^1]$^+$ where Li$^+$ is in the centre of the cryptand cavity and within 2.081(6) Å of the oxygen in the –N(CH$_2$)$_2$-O(CH$_2$)$_2$N– segments of L^1, but is less expected for exclusive [NaL^1]$^+$. However, in the crystal structure[4] of [NaL^1(NCS)], in which Na$^+$ is sited above the 15-membered ring of L^1 delineated by two nitrogens and three oxygens, the fourth and most distant L^1 oxygen is only 2.662(9) Å from Na$^+$ [which compares with 2.289(14), 2.324(13), and 2.443(19) Å from the three oxygens in the 15-membered ring], and a similar distance is expected to apply in solution. The binding interaction between the fourth oxygen and Na$^+$ will be at its greatest at this distance, and hence it seems that the slowest step in the dissociation of Na$^+$ from exclusive [NaL^1]$^+$ occurs early in the stepwise process, as other evidence has also suggested.[7] (There are insufficient data available to make similar deductions for [NaL^3]$^+$.)

It also appears that the slowest step occurs at an early stage in the dissociation of [LiL^1]$^+$ and [LiL^3]$^+$, but here this slow step probably involves a change from the inclusive to the exclusive form of the cryptate and a greater contribution to $\Delta G^‡$ arising from conformational changes in the cryptand. (This mechanistic proposal is supported by Liesegang's stopped-flow calorimetric study of the formation of [LiL^1]$^+$ in water in which the slower of the two observed reactions is identified as the interconversion of the exclusive and inclusive cryptates.[17])

The lesser sensitivity of k_f to the replacement of an oxygen in L^1 by a methylene group in L^3 indicates that the interaction of the metal ion with the fourth oxygen in the L^1 cryptates makes a smaller contribution to $\Delta G^‡$ characterising the slowest formation step than does the disruption of this interaction in the dissociation process.

As solvational changes can be important in the energetics of cryptate formation[7,16,18] it will be necessary to investigate this process in a range of solvents to consolidate the understanding of the effect of the replacement of an oxygen in L^1 by a methylene group in L^3 on the dynamics of cryptate formation.

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* It is probable that significant, but very labile, contact ion pairing occurs between the counter ion and the surface of Na$^+$ not bound by the cryptand in exclusive [NaL]$^+$, but as both the number of such contact sites available and the ability of the counter ion to compete with solvent for them are uncertain no indication of the occupancy of these sites in solution is shown in the formula [NaL]$^+$.

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