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Structures of isomeric substituted 14-crown-4 ethers and their LiSCN complexes

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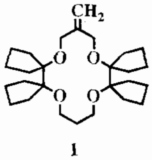
Abstract

Crystal structures of methyleno,tetracyclopentyl-14-crown-4 (**1**), methyl,tetracyclopentyl-14-crown-4 (**2**), methyleno,didecalino-14-crown-4 (**3**), methyl,didecalino-14-crown-4 (**4**), **2**·LiSCN and **4**·LiSCN were determined by X-ray diffraction methods. The free ligands, **2** and **4**, have their rings collapsed, but on complexation open up to accommodate an Li^+ ion. It is bonded to all four O atoms of the crown in each case and to an apical SCN^- ion to form a rectangular pyramid. The methyl group is pseudoaxial in **2**·LiSCN and pseudoequatorial in **4**·LiSCN. In **2** and **4** the bridging propylene groups are disordered over two sites.

Keywords: Crystal structures; Crown ether complexes; Lithium complexes

1. Introduction

Substituted crown ethers of the 14-crown-4 type have been shown to be selective ionophores for the Li^+ ion [1–11]. Because steric effects are clearly important in determining the selectivity, we have studied the molecular geometries of known crowns and their complexes by crystal-structure analyses as well as the syntheses and structural analyses of new crowns with various substituents [12]. We, and others [13], have shown that dibenzo-14-crown-4 is preorganized for complexation, while octamethyl- and dicyclohexano-14-crown-4 [14] ligands change conformation on complexation with Li^+ ions. We have now extended this study to crowns **1–4** bearing substituents which introduce additional steric and conformational constraints, in order to assess how they affect the preorganization of the ligands and the complexation of Li^+ ions. All four ligands and the LiSCN complexes of **2** and **4** were analyzed by X-ray diffraction to determine their crystal and molecular structures.



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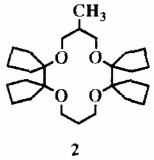

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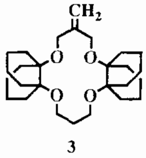

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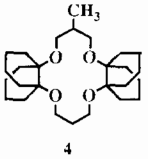

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2. Experimental

2.1. Synthesis

An efficient synthesis of these ligands from tertiary and neopentyl diols has been reported previously [15]. The closure of the ring by use of methallyl dichloride results in the incorporation of a methyleno substituent in **1** and **3**. This can be reduced to a methyl group to form **2** and **4**. Complexes of the latter compounds were made by reacting them with stoichiometric amounts of LiSCN. Suitable crystals for X-ray diffraction of all six compounds were grown by evaporation of ethanol solutions.

2.2. X-ray diffraction

The crystal structures of **1–4**, **2**·LiSCN and **4**·LiSCN were determined by X-ray diffraction methods. Intensity data for all compounds were collected with an Enraf Nonius CAD4 diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å). The treatment of the data was the same as described previously [12]. In each case the structure was determined by use of MULTAN 82 [16] and Fourier methods, and was refined by least-squares. Hydrogen atoms in cal-

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Table 1
Crystal data and structure dctermination information for compounds **1**, **2**, **3**, **4**, **2**·LiNCS and **4**·LiNCS

	1	**2**	**3**	**4**	**2**·LiNCS	**4**·LiNCS
Formula	$C_{27}H_{44}O_4$	$C_{27}H_{46}O_4$	$C_{27}H_{44}O_4$	$C_{27}H_{46}O_4$	$C_{28}H_{46}O_4NSLi$	$C_{28}H_{46}O_4NSLi$
Formula weight	432.65	434.67	432.65	434.67	499.69	499.69
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic	triclinic
a (Å)	13.350(5)	5.8615(5)	12.413(2)	21.417(8)	12.829(2)	11.197(8)
a (Å)	10.250(2)	8.6524(6)	14.314(2)	10.121(2)	25.625(5)	11.773(8)
c (Å)	9.500(3)	12.861(2)	14.397(3)	12.692(5)	16.723(6)	11.801(6)
α (°)	90.0	80.07(8)	90.0	90.0	90.0	62.98(6)
β (°)	109.47(2)	77.05(8)	110.26(1)	116.54(2)	90.0	80.91(4)
γ (°)	90.0	88.34(6)	90.0	90.0	90.0	88.87(4)
V (Å^3)	1226(1)	626.1(1)	2400(2)	2461(2)	5498(3)	1366(2)
T (K)	298	298	300	296	298	298
Space group	$P2_1/c$ (No. 14)	$P1$ (No. 1)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$Pbca$ (No. 61)	$P\bar{1}$ (No. 2)
Z	2	1	4	4	8	2
Reflections, θ angles	13	25	25	25	24	20
for cell least-squares	7.6–11.5	18.1–20.5	18.1–20.5	7.0–11.5	10.0–13.4	7.0–13.5
D_{calc} (g/cm^3)	1.17	1.15	1.20	1.17	1.21	1.22
Crystal shape	prism	platelet	prism	rod	prism	prism
Crystal size (mm)	0.12×0.29×0.34	0.05×0.15×0.63	0.47×0.51×0.60	0.09×0.14×0.88	0.23×0.27×0.62	0.16×0.18×0.51
Absorption correction	0.957–1.0	0.968–1.0	0.985–1.0	0.928–1.0	0.944–1.0	0.940–1.0
Range of 2θ (°)	<48	<46	<48	<44	<40.4	<46
Range of hkl	0, 10; 0, 11; ±15	0, 6; ±9; ±14	0, 14; 0, 16; ±16	0, 22; 0, 10; ±13	0, 12; 0, 24; 16	0, 12; ±12; ±12
Observed reflections	807 $I>\sigma(I)$	1302 $I>\sigma(I)$	2565 $I>\sigma(I)$	704 $I>2\sigma(I)$	1588 $I>\sigma(I)$	2812 $I>\sigma(I)$
No. variables	145	320	280	143	316	316
$R(F)$	0.056	0.063	0.047	0.062	0.057	0.050
R_w	0.069	0.080	0.066	0.074	0.078	0.065
GOF	1.87	2.66	1.98	1.88	2.45	1.79
$(\rho_o-\rho_c)$ (e/Å^3)	−0.15, +0.12	−0.20, +0.15	−0.18, +0.29	−0.24, +0.33	−0.21, +0.21	−0.32, +0.39

Table 2
Positional and isotropic equivalent thermal parameters for methyleno,tetracyclopentyl-14-crown-4 (**1**)

Atom	x	y	z	B_{eq} (Å^2)
O(1)	0.3556(2)	0.1258(3)	0.9583(3)	4.13(7)
O(4)	0.3112(2)	−0.1515(3)	0.8803(3)	4.27(7)
C(2)	0.2669(3)	0.0555(4)	0.9769(4)	3.8(1)
C(3)	0.2373(3)	−0.0436(4)	0.8480(4)	3.7(1)
C(5)	0.4117(3)	−0.1343(5)	0.8638(5)	5.3(1)
C(13)	0.5162(3)	0.2449(4)	1.0609(5)	4.4(1)
C(14)	0.4048(3)	0.2257(5)	1.0645(5)	5.0(1)
C(15)	0.2967(3)	−0.0125(5)	1.1296(4)	5.4(1)
C(16)	0.2370(4)	0.0633(7)	1.2178(5)	7.6(2)
C(17)	0.1384(3)	0.1087(6)	1.1001(5)	6.6(1)
C(18)	0.1752(3)	0.1489(5)	0.9721(4)	4.8(1)
C(19)	0.1307(3)	−0.1126(5)	0.8188(5)	4.7(1)
C(20)	0.0991(4)	−0.1624(6)	0.6610(5)	7.3(2)
C(21)	0.1620(4)	−0.0855(6)	0.5826(5)	6.5(1)
C(22)	0.2254(3)	0.0149(4)	0.6954(4)	4.4(1)
C(31)[a]	0.5437(7)	0.346(1)	1.020(1)	5.6(3)

[a] Occupancy factor 0.5.

culated positions were included and were given isotropic thermal parameters equivalent to those of the carbon atoms to which they are bonded.

There is disorder in the crystals of **1**, **2** and **4**. Molecules of **1** lie on crystallographic centers of symmetry, a fact which requires disorder, with the methyleno groups extending from the ring on opposite sides with about equal probability. In the structure of **2** there is disorder in the propylene groups, with a major conformation A and a minor one B. In addition, the methyl group has four possible sites. Because of this extensive disorder, this structure is the least well determined of the six. Crystal symmetry requires that, on average, molecules of **4** are centrosymmetric; this is achieved by the propylene groups, with and without the CH_3, partially occupying sites on both sides of the molecule in a random manner.

The crystal data and information relevant to the structure determination and the least-squares refinement are given in Table 1. It will be noted that the ratio of data to parameters is small in several cases. This is because these crystals are difficult to grow, and small, weakly scattering specimens had to be used. Positional and isotropic equivalent thermal parameters are listed in Tables 2–7. Selected bond distances and angles are given in Table 8; see also Supplementary material.

3. Results and discussion

The molecular configuration of each ligand and complex is shown in Fig. 1(a)–(f). The free ligands **1–4**

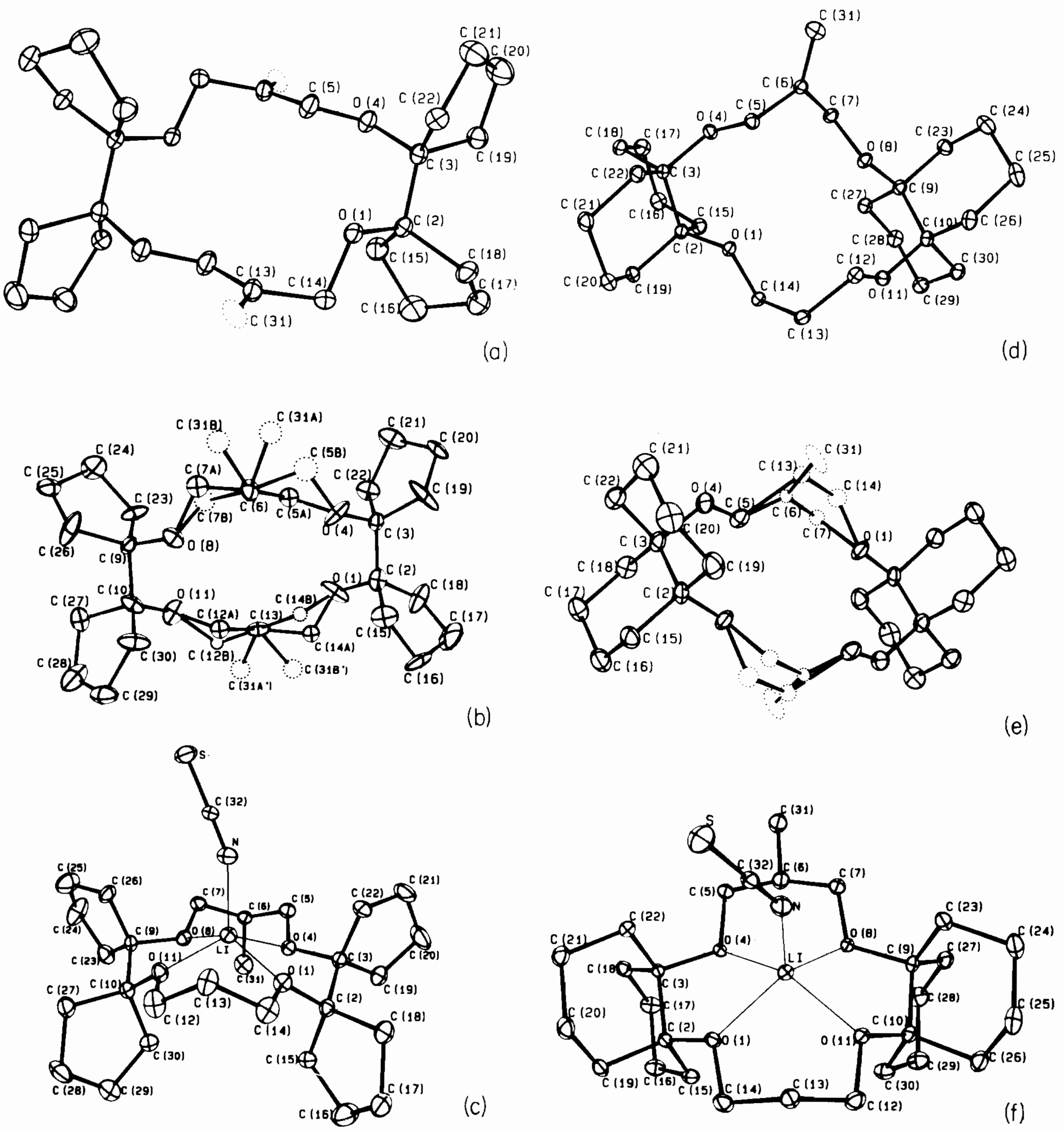

Fig. 1. Structures of the ligands and complexes as follows: (a) **1**, (b) **2**, (c) **2**·LiNCS, (d) **3**, (e) **4**, (f) **4**·LiNCS. Atoms are represented by 10% probability thermal ellipsoids, and partially occupied sites are dotted. Hydrogen atoms are omitted.

have conformations of the 14-crown-4 ring that are similar to each other but different from that in the complexes with LiSCN. In the former the ring is collapsed, with the O atoms in contact with each other in pairs; but when a complex forms, the ring opens up, and the Li^+ ion is partially inserted into the cavity of the macrocycle. In this position it is bonded to the four O atoms of the ether and lies 0.65 Å from their plane; a SCN^- ion completes the five-coordination of the Li^+ ion. This conformation is essentially the same as in Li complexes of nonamethyl-, dibenzo- and dicyclohexano-14-crown-4. In dibenzo-14-crown-4 the ring

Table 3
Positional and isotropic thermal parameters for methyl, tetracyclopentyl-14-crown-4 (**2**)

Atom	x	y	z	B_{eq} (Å^2)
O(1)	0.3988(8)	0.2959(6)	0.7065(4)	8.7(1)
O(4)	0.1054(7)	0.0402(5)	0.6970(4)	8.5(1)
O(8)	−0.0578(7)	−0.0285(5)	1.0226(3)	6.1(1)
O(11)	0.2186(7)	0.2241(5)	1.0481(4)	6.3(1)
C(2)	0.291(1)	0.2862(8)	0.6174(5)	5.4(2)
C(3)	0.296(1)	0.1053(7)	0.6117(4)	4.8(1)
C(5A)^a	0.147(2)	−0.031(1)	0.7836(7)	4.6(2)
C(5B)	0.056(4)	−0.114(3)	0.761(2)	11.2(7)
C(6)	−0.092(1)	−0.1030(7)	0.8607(5)	5.9(1)
C(7A)	−0.073(2)	−0.152(1)	0.9629(9)	6.1(3)
C(7B)	0.067(2)	−0.094(2)	0.957(1)	3.8(3)
C(9)	0.026(1)	−0.0237(7)	1.1164(4)	5.0(1)
C(10)	0.039(1)	0.1446(7)	1.1231(5)	5.2(1)
C(12A)	0.176(2)	0.304(1)	0.9550(7)	5.8(2)
C(12B)	0.303(2)	0.360(1)	0.9722(9)	5.3(3)
C(13)	0.427(1)	0.3666(7)	0.8751(5)	5.5(2)
C(14A)	0.401(2)	0.416(1)	0.7641(6)	4.6(2)
C(14B)	0.260(3)	0.323(2)	0.792(1)	5.5(4)
C(15)	0.053(1)	0.3637(8)	0.6268(6)	6.4(2)
C(16)	0.095(1)	0.5155(8)	0.5577(6)	8.3(2)
C(17)	0.320(2)	0.503(1)	0.4746(7)	11.2(3)
C(18)	0.440(1)	0.396(1)	0.5299(6)	7.8(2)
C(19)	0.247(1)	0.065(1)	0.5056(5)	11.0(2)
C(20)	0.389(2)	−0.0505(9)	0.4709(5)	9.3(2)
C(21)	0.537(1)	−0.0976(9)	0.5538(8)	8.5(2)
C(22)	0.529(1)	0.0358(7)	0.6101(6)	6.6(2)
C(23)	0.276(1)	−0.0935(8)	1.1142(7)	7.5(2)
C(24)	0.238(1)	−0.269(1)	1.1762(7)	8.5(2)
C(25)	0.024(1)	−0.2525(9)	1.2616(6)	7.5(2)
C(26)	0.137(2)	−0.118(1)	1.2256(7)	11.2(3)
C(27)	0.088(1)	0.160(1)	1.2345(6)	8.1(2)
C(28)	0.034(2)	0.309(1)	1.2593(9)	12.6(3)
C(29)	0.211(2)	0.3602(9)	1.1931(7)	8.6(2)
C(30)	0.205(1)	0.2302(9)	1.1169(7)	7.8(2)
C(31A′)^b	0.514(3)	0.485(2)	0.923(1)	3.3(3)^c
C(31A)	0.138(4)	−0.248(3)	0.810(2)	6.7(5)^c
C(31B)	0.197(7)	−0.282(5)	0.907(3)	6.0(9)^c
C(31B′)	0.556(6)	0.521(4)	0.813(3)	5.2(7)^c

[a] Occupancy factors for structures A and B are 0.63 and 0.37, respectively, except for atom C(31).

[b] Occupancy factors are 0.315 for C(31A) and C(31A′) and 0.185, for C(31B) and C(31B′).

[c] Isotropic thermal parameters.

Table 4
Positional and isotropic equivalent thermal parameters for methyleno,didecalino-14-crown-4 (**3**)

Atom	x	y	z	B_{eq} (Å^2)
O(1)	0.1427(1)	0.1753(1)	0.0270(1)	2.79(3)
O(4)	0.1051(1)	0.1843(1)	0.2067(1)	2.83(4)
O(8)	0.4142(1)	0.1509(1)	0.25412(9)	2.80(3)
O(11)	0.4519(1)	0.1577(1)	0.0737(1)	2.94(3)
C(2)	0.0581(2)	0.2414(2)	0.0353(2)	2.65(5)
C(3)	0.0122(2)	0.1962(2)	0.1129(2)	2.57(5)
C(5)	0.1689(2)	0.0989(2)	0.2268(2)	2.78(5)
C(6)	0.2701(2)	0.1131(2)	0.3194(1)	2.54(5)
C(7)	03559(2)	0.1851(2)	0.3171(2)	3.06(5)
C(9)	0.5103(2)	0.2053(2)	0.2487(2)	2.72(5)
C(10)	0.5451(2)	0.1553(2)	0.1676(2)	2.68(5)
C(12)	0.3680(2)	0.0849(2)	0.0476(2)	2.94(5)
C(13)	0.2730(2)	0.1164(2)	−0.0459(2)	3.09(5)
C(14)	0.2085(2)	0.2013(2)	−0.0330(2)	2.97(5)
C(15)	0.1132(2)	0.3362(2)	0.0718(2)	3.37(6)
C(16)	0.0333(2)	0.4033(2)	0.0997(2)	3.97(6)
C(17)	−0.0099(2)	0.3590(2)	0.1759(2)	4.03(6)
C(18)	−0.0671(2)	0.2652(2)	0.1396(2)	3.38(6)
C(19)	−0.0392(2)	0.2498(2)	−0.0657(2)	3.31(6)
C(20)	−0.0958(2)	0.1558(2)	−0.1019(2)	3.69(6)
C(21)	−0.1436(2)	0.1132(2)	−0.0274(2)	3.66(6)
C(22)	−0.0493(2)	0.1044(2)	0.0743(2)	3.12(5)
C(23)	0.6091(2)	0.2003(2)	0.3490(2)	3.40(6)
C(24)	0.6475(2)	0.1003(2)	0.3795(2)	4.50(7)
C(25)	0.6813(2)	0.0511(2)	0.3008(2)	4.89(7)
C(26)	0.5852(2)	0.0557(2)	0.1991(2)	3.61(6)
C(27)	0.4746(2)	0.3060(2)	0.2193(2)	3.16(5)
C(28)	0.5672(2)	0.3622(2)	0.1957(2)	3.79(6)
C(29)	0.6035(2)	0.3130(2)	0.1176(2)	3.85(6)
C(30)	0.6393(2)	0.2126(2)	0.1464(2)	3.46(6)
C(31)	0.2832(2)	0.0637(2)	0.4003(2)	4.25(7)

Table 5
Positional and isotropic equivalent thermal parameters for methyl,didecalino-14-crown-4 (**4**)

Atom	x	y	z	B_{eq} (Å^2)
O(1)	0.3948(2)	0.5671(3)	−0.0940(3)	5.1(1)
O(4)	0.5183(2)	0.2190(3)	0.0266(3)	4.64(9)
C(2)	0.6362(2)	0.3095(5)	0.0907(4)	4.2(1)
C(3)	0.5901(2)	0.2090(5)	0.1144(4)	4.0(1)
C(5)	0.4738(2)	0.3146(5)	0.0340(4)	4.5(1)
C(6)	0.4179(4)	0.3494(9)	−0.0508(7)	2.3(2)^a
C(7)	0.3754(4)	0.460(1)	−0.0342(8)	3.5(2)^a
C(13)	0.4087(4)	0.3245(9)	−0.1156(8)	3.7(2)^a
C(14)	0.3637(5)	0.443(1)	−0.1066(9)	4.9(3)^a
C(15)	0.7107(2)	0.3033(6)	0.1849(4)	5.3(2)
C(16)	0.7168(3)	0.3243(6)	0.3088(5)	6.2(2)
C(17)	0.6732(3)	0.2216(6)	0.3336(5)	6.1(2)
C(18)	0.5974(3)	0.2264(6)	0.2393(4)	5.4(2)
C(19)	0.6318(3)	0.2843(6)	−0.0334(5)	6.3(2)
C(20)	0.6478(3)	0.1421(7)	−0.0512(5)	7.1(2)
C(21)	0.6023(3)	0.0467(7)	−0.0268(5)	6.5(2)
C(22)	0.6084(3)	0.0683(5)	0.0959(5)	5.2(2)
C(31)	0.4069(7)	0.307(1)	−0.1741(9)	8.1(4)

[a] Each of these atoms is disordered over two sites related by a center of symmetry and have equal occupancy. They are assigned isotropic thermal parameters.

is preorganized, but in all the others a rearrangement of the crown occurs on complexation. From the solvent-extraction studies [15] it appears that preorganization is not a dominant factor, since the nonamethyl, dideclino and dicyclohexano derivatives, none of which is preor-

Table 6
Positional and isotropic equivalent thermal parameters for methyl,tetracyclopentyl-14-crown-4 · LiSCN (**2** · LiSCN)

Atom	x	y	z	B_{eq} (Å^2)
S	0.3576(2)	0.13684(7)	0.3799(1)	7.72(6)
O(1)	0.5812(3)	0.1253(1)	0.6926(2)	4.10(9)
O(4)	0.6743(3)	0.2001(1)	0.6212(2)	3.88(9)
O(8)	0.7398(3)	0.1309(1)	0.4986(2)	4.15(9)
O(11)	0.6527(3)	0.0535(1)	0.5671(2)	4.40(9)
N	0.4889(4)	0.1431(2)	0.5087(3)	6.2(1)
C(2)	0.6274(4)	0.1634(2)	0.7439(3)	3.6(1)
C(3)	0.6194(4)	0.2141(2)	0.6952(3)	4.1(1)
C(5)	0.6817(5)	0.2393(2)	0.5594(3)	4.7(2)
C(6)	0.7682(5)	0.2242(2)	0.5020(3)	4.2(1)
C(7)	0.7428(5)	0.1778(2)	0.4497(3)	5.0(2)
C(9)	0.7559(4)	0.0811(2)	0.4597(3)	3.7(1)
C(10)	0.7541(4)	0.0442(2)	0.5305(3)	3.9(1)
C(12)	0.6097(5)	0.0157(2)	0.6206(4)	6.3(2)
C(13)	0.5158(5)	0.0397(2)	0.6614(4)	5.2(2)
C(14)	0.5427(5)	0.0776(2)	0.7256(4)	6.1(2)
C(15)	0.7391(5)	0.1487(2)	0.7651(4)	4.9(2)
C(16)	0.7472(6)	0.1430(4)	0.8534(4)	9.0(3)
C(17)	0.6390(6)	0.1386(3)	0.8854(4)	6.7(2)
C(18)	0.5709(5)	0.1688(2)	0.8258(3)	5.1(2)
C(19)	0.6713(5)	0.2624(2)	0.7351(4)	5.3(2)
C(20)	0.5931(6)	0.3060(3)	0.7384(5)	8.9(2)
C(21)	0.5048(7)	0.2907(3)	0.6887(5)	9.9(2)
C(22)	0.5070(5)	0.2308(3)	0.6782(4)	5.7(2)
C(23)	0.8602(5)	0.0806(3)	0.4137(4)	5.9(2)
C(24)	0.8317(7)	0.0765(4)	0.3259(4)	10.3(3)
C(25)	0.7246(7)	0.0565(4)	0.3206(4)	9.2(3)
C(26)	0.6731(5)	0.0699(2)	0.3966(3)	5.4(2)
C(27)	0.7678(5)	−0.0152(2)	0.5054(4)	5.4(2)
C(28)	0.8474(5)	−0.0376(3)	0.5629(5)	8.1(2)
C(29)	0.8934(6)	0.0029(3)	0.6098(5)	8.4(2)
C(30)	0.8406(5)	0.0533(2)	0.5919(4)	5.3(2)
C(31)	0.8719(5)	0.2186(3)	0.5429(4)	6.7(2)
C(32)	0.4325(4)	0.1403(2)	0.4558(3)	4.3(1)
Li	0.6174(7)	0.1298(4)	0.5764(6)	3.9(2)

Table 7
Positional and isotropic equivalent thermal parameters for methyl,didecalino-14-crown-4 · LiSCN (**4** · LiSCN)

Atom	x	y	z	B_{eq} (Å^2)
S	−0.1960(1)	0.01237(8)	0.18680(8)	5.85(3)
O(1)	0.3590(2)	−0.3316(2)	0.6684(2)	2.69(4)
O(4)	0.1377(2)	−0.3809(2)	0.6645(1)	2.59(4)
O(8)	0.1499(2)	−0.1909(2)	0.4091(1)	2.79(4)
O(11)	0.3725(2)	−0.1317(2)	0.3947(1)	2.83(4)
N	−0.2033(2)	0.0844(2)	0.3820(2)	4.30(7)
C(2)	0.3173(2)	−0.4646(2)	0.7458(2)	2.54(6)
C(3)	0.1788(2)	−0.4614(2)	0.7862(2)	2.36(6)
C(5)	0.0108(3)	−0.3604(3)	0.6735(3)	4.30(9)
C(6)	−0.0313(3)	−0.3078(4)	0.5505(3)	5.6(1)
C(7)	0.0223(3)	−0.1881(3)	0.4433(3)	4.23(9)
C(9)	0.2061(3)	−0.0933(2)	0.2823(2)	3.00(7)
C(10)	0.3417(3)	−0.1214(2)	0.2754(2)	2.97(7)
C(12)	0.4989(3)	−0.1348(3)	0.4049(3)	3.94(8)
C(13)	0.5128(3)	−0.1649(3)	0.5400(3)	3.29(7)
C(14)	0.4874(3)	−0.3031(3)	0.6384(3)	3.93(8)
C(15)	0.3433(3)	−0.5341(3)	0.6628(3)	3.36(7)
C(16)	0.2807(3)	−0.6673(3)	0.7251(3)	4.27(8)
C(17)	0.1453(3)	−0.6617(3)	0.7610(3)	4.20(8)
C(18)	0.1191(3)	−0.5964(2)	0.8470(3)	3.18(7)
C(19)	0.3771(3)	−0.5267(3)	0.8671(3)	3.38(7)
C(20)	0.3495(3)	−0.4638(3)	0.9553(3)	4.26(8)
C(21)	0.2137(3)	−0.4631(3)	0.9945(2)	3.92(8)
C(22)	0.1518(3)	−0.3997(2)	0.8760(2)	3.03(7)
C(23)	0.1861(3)	0.0380(3)	0.2761(3)	4.13(8)
C(24)	0.2639(4)	0.1456(3)	0.1600(3)	5.6(1)
C(25)	0.3975(4)	0.1178(3)	0.1577(3)	5.4(1)
C(26)	0.4176(3)	−0.0110(3)	0.1587(3)	4.10(8)
C(27)	0.1545(3)	−0.1078(3)	0.1769(3)	4.00(8)
C(28)	0.1734(3)	−0.2363(3)	0.1795(3)	4.73(8)
C(29)	0.3069(3)	−0.2611(3)	0.1679(3)	4.77(8)
C(30)	0.3620(3)	−0.2487(3)	0.2726(3)	3.89(8)
C(31)	−0.1689(3)	−0.3027(4)	0.5723(3)	6.4(1)
C(32)	−0.2003(3)	0.0540(2)	0.3012(3)	3.22(7)
Li	0.2447(4)	−0.2140(4)	0.5517(4)	2.9(1)

ganized, are more selective of Li$^+$ ions than is dibenzo-14-crown-4.

In the uncomplexed ligands **2** and **4** there is disorder in the propylene bridges, although the methylene bridges and their attached bulky substituents are ordered. When the O atoms become bonded to the Li$^+$ ion, a new conformation is achieved, and the propylene bridges are each locked into just one position, i.e. the disorder disappears. Studies of **2** and **4** in solution by variable-temperature NMR have shown that two conformations exist in each case [17]. In crystals of both of the complexes the 14-crown-4 ring has a pseudo-chair conformation, while the methyl substituent is axial in **2** · LiSCN and equatorial in **4** · LiSCN. This moiety is not in contact with the SCN$^-$ ion in either of these molecules.

These studies, along with those reported earlier [12], show the type of complexes that are formed with these ligands as well as the conformational changes that occur upon complexation. Nevertheless, they do not show any obvious correlation with the observed solvent-extraction selectivity [15]. Among the 14-crown-4 ligands studied by us [15] the most selective for Li$^+$ extraction is nonamethyl-14-crown-4, which is flexible, not preorganized, and has substituents of only moderate bulk. Information about the rigidity, preorganization, and bulkiness of the ligands provide important, but limited, predictive power regarding complexation and selectivity in separating Li$^+$ ions from the other alkali metal cations in solution.

Table 8
Individual and averaged bond lengths (Å) and angles (°)

	Compound					
	1	**2**	**3**	**4**	**2**·LiSCN	**4**·LiSCN
Bond type						
$C{=}CH_2$	1.21(1)		1.323(3)			
$C–CH_3$		1.54(8)		1.54(1)	1.502(9)	1.526(5)
C–O	1.43(1)	1.37(7)	1.44(1)	1.43(4)	1.45(1)	1.44(1)
C–C	1.52(5)	1.52(8)	1.53(1)	1.53(5)	1.51(2)	1.52(1)
Li–O					2.03(3)	2.04(2)
Li–N					2.03(1)	2.023(5)
C=N					1.146(8)	1.157(5)
C–S					1.594(6)	1.626(4)
Angle type						
O(1)–C(2)–C(3)	103.7(3)	103.6(5)	104.0(2)	103.1(4)	103.3(4)	104.6(2)
C(2)–C(3)–O(4)	111.1(3)	104.2(4)	110.2(2)	111.0(4)	102.2(4)	103.6(2)
C(3)–O(4)–C(5)	119.1(3)	119.2(6)	119.7(2)	121.5(4)	117.7(4)	115.7(2)
O(4)–C(5)–C(6)		109.1(7)	107.5(2)	124.0(6)	108.9(4)	113.7(2)
C(5)–C(6)–C(7)		112.9(7)	117.4(2)	119.5(7)	114.1(5)	121.2(3)
C(6)–C(7)–O(8)		114.8(7)	107.5(2)	98.4(8)	109.3(4)	112.6(2)
C(7)–O(8)–C(9)		132.6(6)	117.3(2)		118.2(4)	116.6(2)
O(8)–C(9)–C(10)		105.4(4)	104.0(2)		101.4(4)	103.9(2)
C(9)–C(10)–O(11)		113.7(4)	110.6(2)		103.8(4)	104.7(2)
C(10)–O(11)–C(12)		119.1(6)	120.2(2)		119.7(4)	117.0(2)
O(11)–C(12)–C(13)		108.2(8)	106.7(2)		108.2(5)	109.7(2)
C(12)–C(13)–C(14)	111.7(4)	110.8(7)	114.5(2)		114.0(5)	115.4(3)
C(13)–C(14)–O(1)	107.5(4)	115.2(6)	107.8(2)	114.7(9)	111.1(5)	108.8(2)
C(14)–O(1)–C(2)	118.2(3)	130.4(6)	117.5(2)	125.8(9)	119.7(4)	117.0(2)
C(5)–C(6)–C(31)	121.8(6)	103.3(9)	121.4(2)	116.8(9)	112.6(5)	109.5(3)
S–C(32)–N					177.9(5)	179.6(2)
C–C–C(decalino)			111(1)	111(1)		111(1)
C–C–C(cyclopentyl)	105(1)	106(3)			107(2)	

4. Supplementary material

Complete lists of bond distances and angles, anisotropic thermal parameters, calculated H atom positions, and structure factors may be obtained from the authors.

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