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Crystal Structure Analyses of 1,4,7,10,13,16-Hexaoxacyclooctadecane and its Complexes with Lithium Perchlorate Dihydrate and Lithium Thiocyanate Dihydrate at −150 °C

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Crystals were grown at room temperature and cooled rapidly to about −150 °C, the temperature at which data were collected on an automatic four-circle diffractometer. The cyclic hexaether of the perchlorate complex adopts the non-angular D_{3d} conformation, while that of the (2:1) thiocyanate complex is the biangular [8, 10]. In both structures the (18-crown-6) ring skeleton, which is too large for the small Li^+ ion, is effectively narrowed by the encapsulated water molecules. They have the double role of acting as coordinating agents towards Li^+ and hydrogen bond donors towards the ether oxygens, and are creating geometries compatible with the coordination preferences for the lithium cation.

1,4,7,10,13,16-Hexaoxacyclooctadecane (18-crown-6), in its complexes with K^+ and larger cations, adopts a centrosymmetric non-angular D_{3d} conformation [1] [Fig. 1(a)]. This conformation is also found in several crystalline "adducts" or molecular complexes.[2–4] An exception is one involving the NH_2 group of benzenesulfonamid [5] where the cyclic hexaether has the centrosymmetric biangular [99] * conformation shown in Fig. 1(b). In the absence of cations or protic adduct-formers, 18-crown-6 crystallizes in a completely different non-angular centrosymmetric conformation [1] [Fig. 1(c)]. Among the complexes with smaller cations than K^+, that of hydrated sodium thiocyanate has been investigated by X-rays.[1] The crystal structure reveals that a part of the ring is deformed in a highly irregular manner, which brings one ether oxygen into an apical ligand position 1.95 Å out of the mean plane of the other five, giving the triangular [3, 5, 10] conformation illustrated in Fig. 2. In order to explore whether the hexaether may adopt other conformations, compatible with the coordination preferences for

* A shorthand notation for conformational type, consisting of a series of numbers within brackets, each giving the number of bonds in one "side", starting with the shortest. The direction around the ring is so chosen that the following number is smallest possible.

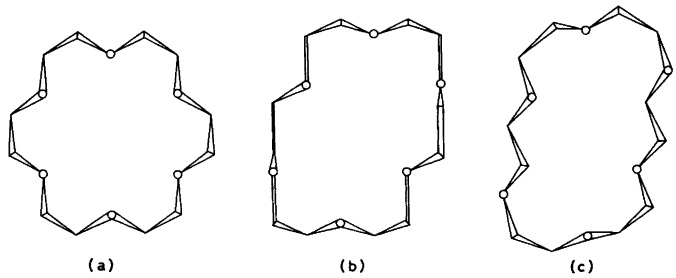

Fig. 1. Crystal structures of 1,4,7,10,13,16-hexaoxacyclooctadecane (a) as a 1:1 complex with KSCN, (b) as a 1:2 complex with benzenesulfonamide and (c) in the uncomplexed state.

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Table 1. Crystal data for $LiClO_4 \cdot (CH_2-CH_2-O)_6 \cdot 2H_2O$ (I) and $(iSCN)_2 \cdot (CH_2-CH_2-O)_6 \cdot 2H_2O$ (II).

	Space group	a (Å)	b (Å)	c (Å)	β(°)	Z	D_m g cm^{-3}	D_x g cm^{-3}	Number of observed reflections
(I)	$P2_1/c$	17.006(2)	7.058(1)	20.849(3)	128.72(9)	4	1.35	1.38	2451
(II)	$P2_1/n$	9.533(4)	16.252(6)	13.855(3)	100.49(3)	4	1.30	1.35	3019

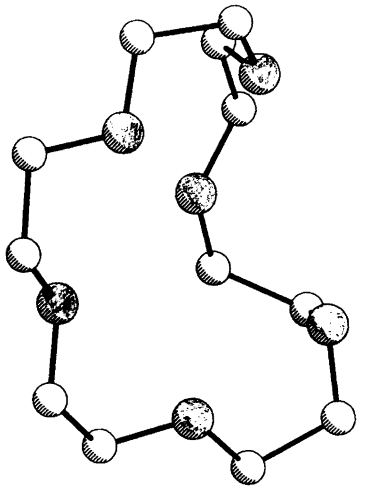

Fig. 2. The conformation of the (18-crown-6) ether in the complex with $NaSCN \cdot H_2O$.

Table 2. Final fractional coordinates with estimated standard deviations for $LiClO_4 \cdot (CH_2CH_2O)_6 \cdot 2H_2O$. Hn1 and Hn2 are bonded to Cn. HWn1 and HWn2 are bonded to OWn.

ATOM	X	Y	Z
O1	.95779(15)	.19546(31)	.82799(12)
O2	.83631(16)	.52934(32)	.73138(13)
O3	.62757(16)	.50520(33)	.62996(13)
O4	.55134(15)	.25203(31)	.67652(12)
O5	.66803(16)	-.07807(30)	.77742(12)
O6	.88242(16)	-.05268(31)	.88776(13)
C1	.99423(24)	.38406(51)	.83619(20)
C2	.93217(25)	.48147(49)	.75452(21)
C3	.77452(26)	.62421(49)	.65405(19)
C4	.67729(25)	.67639(48)	.63675(18)
C5	.53077(26)	.53823(53)	.60841(21)
C6	.48603(24)	.34845(55)	.59974(20)
C7	.51247(24)	.06960(49)	.67266(20)
C8	.57451(25)	-.01988(51)	.75607(20)
C9	.73023(25)	-.17035(50)	.85512(19)
C10	.82730(25)	-.22293(48)	.87345(19)
C11	.97096(24)	-.08886(48)	.89616(19)
C12	1.01886(24)	.09697(50)	.90465(19)
CL	.74365(6)	1.14011(13)	.50375(5)

Table 2. Continued.

O7	.83349(20)	1.22193(43)	.57282(18)
O8A	.67125(48)	1.15095(93)	.51907(41)
O9A	.69249(48)	1.21084(98)	.42292(35)
O10A	.75199(51)	.93038(74)	.49896(36)
O8B	.70112(66)	1.03170(96)	.52852(48)
O9B	.67918(52)	1.29481(92)	.45260(43)
O10B	.77508(51)	1.04815(91)	.46393(33)
OW1	.21810(18)	.69080(32)	.16181(14)
OW2	.24587(17)	.88426(33)	.31032(13)
LI+	.29898(50)	.70072(99)	.27950(37)
HW11	.2556	.7063	.1370
HW12	.1865	.8193	.1442
HW21	.2600	.8600	.3600
HW22	.1800	.8600	.2800
H11	1.0659	.3734	.8582
H12	.9901	.4569	.8751
H21	.9230	.3949	.7123
H22	.9674	.5995	.7583
H31	.7608	.5384	.6099
H32	.8093	.7412	.6563
H41	.6337	.7492	.5841
H42	.6914	.7554	.6827
H51	.4869	.6090	.5553
H52	.5379	.6129	.6526
H61	.4795	.2739	.5559
H62	.4180	.3645	.5850
H71	.5140	-.0129	.6345
H72	.4414	.0832	.6517
H81	.5381	-.1324	.7552
H82	.5866	.0740	.7973
H91	.6957	-.2871	.8535
H92	.7435	-.0829	.8987
H101	.8135	-.2931	.8257
H102	.8675	-.3059	.9235
H111	.9526	-.1570	.8464
H112	1.0189	-.1681	.9461
H121	1.0872	.0745	.9209
H122	1.0252	.1748	.9478

cations too small to fill the ring cavity of the D_{3d} conformation, crystal structure analyses of the complexes (I) and (II) have been carried out.

$$LiClO_4 \cdot (CH_2 \cdot CH_2 \cdot O)_6 \cdot 2H_2O \quad \text{(I)}$$

$$(LiSCN)_2(CN_2 \cdot CH_2 \cdot O)_6 \cdot 2H_2O \quad \text{(II)}$$

Attempts to make a crystalline (1:1) complex with LiSCN were unsuccessful. The crystals of (I) and (II) were grown at room temperature and cooled

Table 3. Final fractional coordinates with estimated standard deviations for $(LiSCN)_2(CH_2CH_2O)_6 \cdot 2H_2O$. Hn1 and Hn2 are bonded to Cn. HWn1 and HWn2 are bonded to OWn.

ATOM	X	Y	Z
O1	1.21353(13)	.08299(7)	.31287(9)
O2	.97310(13)	.11503(7)	.23233(9)
O3	.75311(13)	-.02572(7)	.25739(9)
O4	.85546(13)	-.13582(7)	.64292(9)
O5	1.10904(12)	-.10744(7)	.56389(8)
O6	1.27975(12)	.04038(7)	.62778(8)
C1	1.17791(20)	.13240(11)	.38984(13)
C2	1.04154(20)	.10071(12)	.91484(13)
C3	.73972(20)	.09753(11)	.85415(13)
C4	.75509(20)	.00749(12)	.35385(13)
C5	.69840(20)	-.10978(11)	.75136(14)
C6	.70976(20)	-.14276(11)	.65277(14)
C7	.89314(20)	-.18341(11)	.56407(13)
C8	1.05251(20)	-.18756(11)	.57316(13)
C9	1.26139(19)	-.10637(11)	.58903(13)
C10	1.31360(19)	-.02324(12)	.56440(13)
C11	1.38566(19)	.04771(11)	.71547(13)
C12	1.33992(19)	.11156(12)	.78130(13)
S1	.08664(5)	.39875(2)	.56458(3)
S2	.46203(5)	.23633(3)	.58897(3)
N1	.07235(17)	.25724(10)	.67956(12)
N2	.75032(18)	.19123(10)	.64257(12)
C13	.07999(18)	.31544(11)	.63212(13)
C14	.63137(22)	.21037(11)	.62040(13)
LI1+	1.05536(33)	.03398(19)	.29235(23)

Table 3. Continued.

LI2+	.45034(35)	.33910(19)	.20265(23)
OW1	.00647(12)	.39272(7)	.36926(8)
OW2	.92110(13)	.08285(8)	.19085(10)
HW11	-.0877	.9447	.3666
HW12	.0450	.9269	.4299
HW21	.9821	.1359	.1663
HW22	.8320	.0666	.1676
H11	1.1653	.1909	.9674
H12	1.2557	.1291	.9486
H21	1.0202	.1304	.9739
H22	1.0500	.0404	.9291
H31	.7148	.1258	.8041
H32	.7858	.1204	.9208
H41	.6592	-.0002	.8724
H42	.8289	-.0218	.9024
H51	.5963	-.1084	.7597
H52	.7557	-.1432	.8042
H61	.6480	-.1105	.5998
H62	.6796	-.2018	.6481
H71	.8542	-.1565	.4999
H72	.8531	-.2402	.5650
H81	1.0810	-.2267	.5296
H82	1.0918	-.2068	.6463
H91	1.3021	-.1500	.5505
H92	1.2922	-.1178	.6607
H101	1.2683	-.0023	.4954
H102	1.4195	-.0256	.5698
H111	1.4788	.0642	.6977
H112	1.3969	-.0065	.7504
H121	1.3193	.1645	.7444
H122	1.4172	.1295	.8395

rapidly to about −150 °C, the temperature at which data were collected on an automatic four-circle diffractometer (Mo$K\alpha$-radiation, $2\theta_{max}=50°$). Crystal data for the two compounds are given in Table 1. No corrections for absorption or secondary extinction were made (maximum crystal size 0.4 × 0.5 × 0.3 mm). The structures were (solved by direct methods[6] and refined by full-matrix least squares technique.[7,*] Weights in least squares were obtained from the standard deviations in intensities, $\sigma(I)$, taken as $\sigma(I)=[C_T+(0.02C_N)^2]^{\frac{1}{2}}$ where C_T is the total number of counts, and C_N the net count. Standard deviations in bond distances and angles

*All programs used (except those for phase determination) are included in this reference.

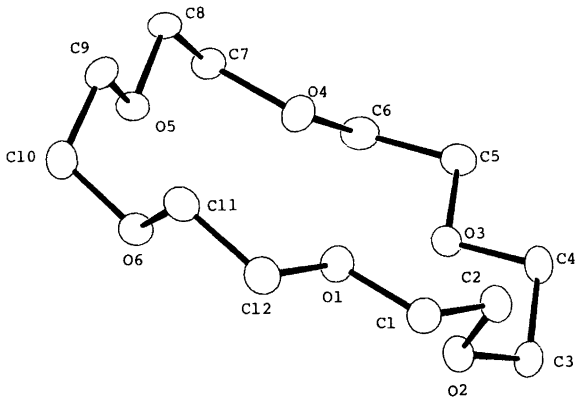

Fig. 3. Schematic drawing showing the [8, 10] conformation of the cyclic hexaether in the complex with $(LiSCN)_2 \cdot 2H_2O$.

Table 4. Bond distances and angles and dihedral angles for $LiClO_4 \cdot (CH_2CH_2O)_6 \cdot 2H_2O$ with estimated standard deviations.

DISTANCE	(Å)	DISTANCE	(Å)
O1 - C1	1.433(4)	O1 - C12	1.428(4)
O2 - C2	1.421(4)	O2 - C3	1.426(4)
O3 - C4	1.430(4)	O3 - C5	1.429(4)
O4 - C6	1.426(4)	O4 - C7	1.426(4)
O5 - C8	1.418(4)	O5 - C9	1.423(4)
O6 - C10	1.436(4)	O6 - C11	1.426(4)
C1 - C2	1.496(5)	C3 - C4	1.501(5)
C5 - C6	1.494(5)	C7 - C8	1.497(5)
C9 - C10	1.490(5)	CL - O7	1.410(3)
CL - O8A	1.455(7)	CL - O9A	1.419(5)
CL -O10A	1.496(5)	CL - O8B	1.357(7)
CL - O9B	1.438(6)	CL -O10B	1.397(5)
OW1 - O9A	2.968(7)	OW1 -O10B	2.877(6)
OW1 - O6	2.882(3)	OW2 - O1	2.852(3)
OW2 - O8A	2.903(7)	OW2 - O8B	2.944(9)
OW1 - LI+	1.922(6)	OW2 - LI+	1.906(7)
LI+ - O3	2.070(7)	LI+ - O4	2.124(7)

ANGLE	(°)	ANGLE	(°)
O1 - C1 - C2	110.3(3)	C1 - O1 - C12	111.2(2)
O1 - C12 - C11	109.5(3)	O2 - C2 - C1	109.8(3)
C2 - O2 - C3	111.9(2)	O2 - C3 - C4	108.0(3)
O3 - C4 - C3	108.1(3)	C4 - O3 - C5	112.8(3)
O3 - C5 - C6	106.9(3)	O4 - C6 - C5	108.2(3)
C6 - O4 - C7	111.1(3)	O4 - C7 - C8	110.5(3)
O5 - C8 - C7	108.9(3)	C8 - O5 - C9	112.3(2)
O5 - C9 - C10	108.7(3)	O6 - C10 - C9	108.6(3)
C10 - O6 - C11	112.2(2)	O6 - C11 - C12	108.2(3)
O7 - CL - O8A	106.2(3)	O7 - CL - O9A	122.4(3)
O7 - CL -O10A	112.7(3)	O7 - CL - O8B	109.7(4)
O7 - CL - O9B	106.4(4)	O7 - CL -O10B	103.0(3)
O8A - CL - O9A	105.6(4)	O8A - CL -O10A	101.3(4)
O9A - CL -O10A	106.4(4)	O8B - CL - O9B	111.7(5)
O8B - CL -O10B	117.2(5)	O9B - CL -O10B	108.0(4)
OW1 - LI+ - OW2	110.1(3)	OW1 - LI+ - O4	105.3(3)
OW2 - LI+ - O3	108.2(3)	OW2 - LI+ - O4	116.1(3)

DIHEDRAL ANGLE	(°)
C11 - C12 - O1 - C1	172.6(3)
C12 - O1 - C1 - C2	177.4(2)
O2 - C2 - C1 - O1	73.2(3)
C3 - O2 - C2 - C1	179.5(3)
C4 - C3 - O2 - C2	-177.5(3)
O3 - C4 - C3 - O2	-63.1(3)
C5 - O3 - C4 - C3	-176.4(3)
C6 - C5 - O3 - C4	177.5(3)
O4 - C6 - C5 - O3	59.3(3)
C7 - O4 - C6 - C5	179.5(3)
C8 - C7 - O4 - C6	-172.8(3)
O5 - C8 - C7 - O4	-73.0(3)
C9 - O5 - C8 - C7	-178.1(3)
C10 - C9 - O5 - C8	-178.8(3)
O6 - C10 - C9 - O5	68.7(3)
C11 - O6 - C10 - C9	-173.1(3)
C12 - C11 - O6 - C10	175.9(3)
O6 - C11 - C12 - O1	-70.3(3)

Table 5. Bond distances and angles and dihedral angles for $(LiSCN)_2(CH_2CH_2O)_6 \cdot 2H_2O$ with estimated standard deviations.

DISTANCE	(Å)	DISTANCE	(Å)
O1 - C1	1.424(2)	O1 - C12	1.431(2)
O2 - C2	1.443(2)	O2 - C3	1.432(2)
O3 - C4	1.439(2)	O3 - C5	1.443(2)
O4 - C6	1.425(2)	O4 - C7	1.435(2)
O5 - C8	1.437(2)	O5 - C9	1.435(2)
O6 - C10	1.431(2)	O6 - C11	1.436(2)
C1 - C2	1.496(3)	C3 - C4	1.506(3)
C5 - C6	1.496(3)	C7 - C8	1.498(3)
C9 - C10	1.506(3)	C11 - C12	1.498(3)
S1 - C13	1.653(2)	S2 - C14	1.648(2)
N1 - C13	1.162(2)	N2 - C14	1.162(2)
LI1+ - OW1	1.966(3)	LI1+ - OW2	1.899(4)
LI1+ - O3	2.073(3)	LI1+ - O4	1.995(3)
LI2+ - OW1	1.996(3)	LI2+ - O2	1.991(3)
LI2+ - N1	2.011(4)	LI2+ - N2	1.998(4)
OW1 - O5	2.803(2)	OW1 - O6	2.755(2)

ANGLE	(°)	ANGLE	(°)
O1 - C1 - C2	108.4(1)	C1 - O1 - C12	112.0(1)
O1 - C12 - C11	108.4(1)	O2 - C2 - C1	108.6(1)
C2 - O2 - C3	112.7(1)	O2 - C3 - C4	113.6(2)
O3 - C4 - C3	109.6(1)	C4 - O3 - C5	110.4(1)
O3 - C5 - C6	108.2(1)	O4 - C6 - C5	107.0(1)
C6 - O4 - C7	114.5(1)	O4 - C7 - C8	108.3(1)
O5 - C8 - C7	109.8(1)	C8 - O5 - C9	111.2(1)
O5 - C9 - C10	108.1(1)	O6 - C10 - C9	113.2(1)
C10 - O6 - C11	112.1(1)	O6 - C11 - C12	109.5(1)
S1 - C13 - N1	178.6(2)	S2 - C14 - N2	179.1(2)

DIHEDRAL ANGLE	(°)
C11 - C12 - O1 - C1	169.3(1)
C12 - O1 - C1 - C2	177.3(1)
O2 - C2 - C1 - O1	-66.7(2)
C3 - O2 - C2 - C1	-171.4(1)
C4 - C3 - O2 - C2	-77.9(2)
O3 - C4 - C3 - O2	-62.4(2)
C5 - O3 - C4 - C3	-171.0(1)
C6 - C5 - O3 - C4	-175.4(1)
O4 - C6 - C5 - O3	56.3(2)
C7 - O4 - C6 - C5	165.3(1)
C8 - C7 - O4 - C6	-165.7(1)
O5 - C8 - C7 - O4	-67.9(2)
C9 - O5 - C8 - C7	172.6(1)
C10 - C9 - O5 - C8	175.4(1)
O6 - C10 - C9 - O5	69.9(2)
C11 - O6 - C10 - C9	86.2(2)
C12 - C11 - O6 - C10	-176.6(1)
O6 - C11 - C12 - O1	65.2(2)

and dihedral angles are calculated from the correlation matrix of the final least squares refinement. Hydrogen atoms were included in the structure factor calculations, but not refined. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Methylene hydrogen positions were calculated while those of the water molecules were localized in difference Fourier maps.

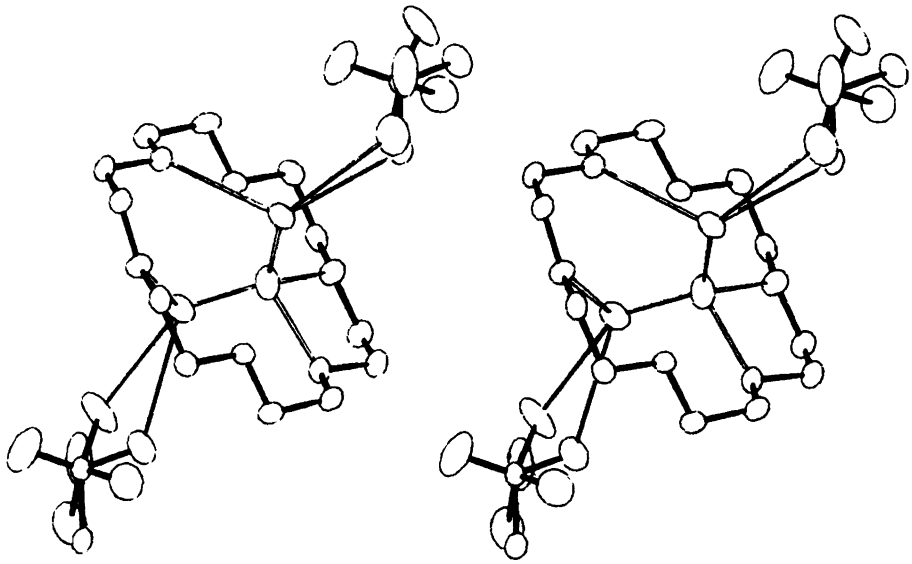

Fig. 4. Stereoscopic view of the complex $LiClO_4 \cdot (CH_2CH_2O)_6 \cdot 2H_2O$.

The final R value for the perchlorate complex was 5.4% ($R_w = 4.8\%$) for 2451 observed reflections. Corresponding values for the thiocyanate complex were $R = 3.0\%$ and $R_w = 3.4\%$ for 3019 observed reflections. Maximum root mean squares anisotropic thermal amplitudes range from 0.17 to 0.40 Å [for (I)] and from 0.15 to 0.22 Å [for (II)].

Final fractional coordinates for (I) are listed in Table 2, and the corresponding values for (II) may be found in Table 3. Bond distances and angles and dihedral angles for (I) and (II), respectively, are given in Table 4 and Table 5.

The torsional angles of Table 4 reveal that the cyclic hexaether of the perchlorate complex adopts the non-angular D_{3d} conformation shown in Fig. 1(a), while those of Table 5 for the thiocyanate complex correspond to the biangular conformation, [8, 10], illustrated in Fig. 3.

Fig. 4 is a stereoscopic view of the complex (I). It may be seen that three oxygens of the perchlorate anion are disordered, and Table 4 shows that these three accept hydrogen bonds from the two water molecules. In addition, two of the crown ether oxygens serve as hydrogen bond acceptors. The

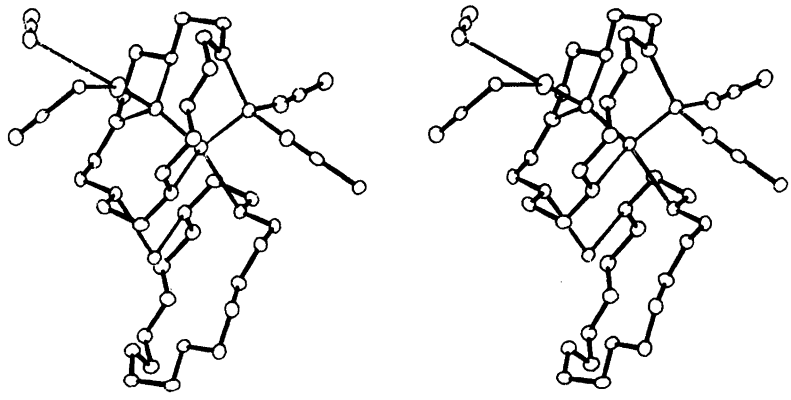

Fig. 5. Stereoscopic view of the complex $(LiSCN)_2(CH_2CH_2O)_6 \cdot 2H_2O$.

lithium cation is coordinated to both water molecules and two ring oxygens. The hydrogen bonds create chains of alternating dihydrated complexes and perchlorate anions.

A stereoscopic view of the (2:1) lithium thiocyanate complex, (II), is presented in Fig. 5. Each lithium cation has four-fold coordination. One is coordinated to two ether oxygens and two water molecules, the other to one ether oxygen, one water molecule and two nitrogens of the thiocyanate anions. Two different ring oxygens in symmetry-related cyclic hexaethers serve as hydrogen bond acceptors for one of the water molecules, while the sulphur atoms of SCN^- accept those of the other. These bonds create a somewhat complicated three-dimensional network.

In both structures the (18-crown-6) ring skeleton, which is too large for the small Li^+ ion, is effectively narrowed by the encapsulated water molecules with the double role of acting as coordinating agents towards Li^+ and hydrogen bond donors towards the ether oxygens. Whether a ring deformation alone, in the absence of any uncharged substrate particles, is able to establish a geometry compatible with the coordination preferences for Li^+, remains to be seen.

Corresponding bond lengths and bond angles of Table 4 and Table 5 do not deviate significantly. They also agree, within error limits, with earlier findings.[1]

Lists of thermal parameters and observed and calculated structure factors are available from the author.

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