12-Crown-3 Type Li⁺ Complexes. Structures of 3,3-Dimethyl-1,5,9-trioxacyclododecane Lithium Perchlorate and 3-Methoxymethyl-3-methyl-1,5,9-trioxacyclododecane Lithium Perchlorate Hemihydrate

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Tinant, B., Declercq, J. P., Fredriksen, S. B. and Dale J., 1993. 12-Crown-3 Type Li⁺ Complexes. Structures of 3,3-Dimethyl-1,5,9-trioxacyclododecane Lithium Perchlorate and 3-Methoxymethyl-3-methyl-1,5,9-trioxacyclododecane Lithium Perchlorate Hemihydrate. – Acta Chem. Scand. 47: 663–667.

The crystal structures of the two title Li⁺ complexes, $C_{11}H_{22}O_3 \cdot LiClO_4$ (III) and $C_{12}H_{24}O_4 \cdot LiClO_4 \cdot 0.5H_2O$ (IV), have been determined by X-ray diffractometry. The structure of III was refined to $R = 0.080$ for 1214 observed reflections, that of IV, with two independent complex entities, to $R = 0.057$ for 1372 reflections. The conformation of the 12-crown-3 ring is the same in III and IV; both follow, as predicted, the diamond lattice, and this is true also for the side-arm in IV. The cation is tetracoordinated in III but, as expected, pentacoordinated for the side-armed ligand IV. The large differences observed in complex stabilities for III and the previously studied complexes, I (the unsubstituted 12-crown-3) and II (the hexamethyl-substituted 12-crown-3), can be correlated to the *gauche* torsion angles in the C–C bonds of the ring, the quaternary carbons introducing conformational rigidity.

A series of novel macrocyclic ligands having ether oxygens in a 1,5-relationship, in order to favour the complexation of small cations (Li^+, Mg^{2+}), have recently been synthesized.[1–3] The stability of their lithium complexes in acetonitrile–methanol (95 : 5) turned out to vary a great deal;[4] in particular, the unsubstituted 12-crown-3 (I) had a complexation constant several orders of magnitude larger than the hexamethyl-substituted 12-crown-3 (II). Nevertheless, the crystal structure of these two Li complexes[1,5,6] revealed essentially the same ring conformation, the same coordination number (four), and no steric interference between the methyl groups of II and the complexed salt ($LiClO_4$).

In order to shed more light on the observed stability difference we have now examined the crystal structures of lithium complexes of two further ligands of this type, the dimethyl-substituted 12-crown-3 (III) and the methoxymethyl, methyl-substituted 12-crown-3 (IV). The latter

contains a fourth ligating ether oxygen in the side-arm, which would be expected to increase the coordination number of Li^+.

Experimental

Crystals were obtained by evaporation from an ethanol–hexane mixture for III, and from an ethyl ether–acetone–hexane mixture for IV. A summary of data collection and refinement parameters is presented in Table 1. For both structures the lattice parameters were refined using 30 reflections in the range $5 \leqslant 2\theta \leqslant 30°$. A Huber four-circle diffractometer, with monochromatized Mo $K\alpha$ radiation, was used for the measurements. One standard reflection was checked every 50 reflections: no significant intensity deviation was observed. Both structures were solved by SHELXS86.[7] All H atom positions were computed riding on the C atoms (C–H = 1.08 Å, $\angle$ H–C–H = 109.5°) except the H atoms of the water molecule in structure IV, which were localized from a difference Fourier. Anisotropic least-squares refinement was carried out with SHELX76[8] using F; H were isotropic with a common refined temperature factor. In structure III the perchlorate anion was disordered, and two positions for each of the oxygen atoms were refined. At the end of the refinement their occupation factors were 0.69

I   II   III   IV

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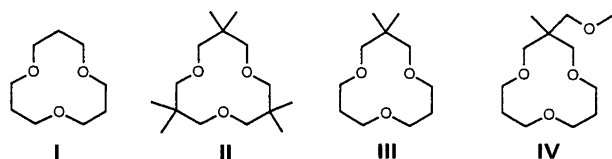
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Table 1. Data collection and refinement parameters.

	III	IV
Formula	$C_{11}H_{22}O_3 \cdot LiClO_4$	$C_{12}H_{24}O_4 \cdot LiClO_4 \cdot 0.5H_2O$
M_r	308.68	347.71
System	Orthorhombic	Orthorhombic
Space group	$Pna2_1$	$Pna2_1$
$a/Å$	16.905(2)	26.614(5)
$b/Å$	10.157(1)	14.711(4)
$c/Å$	9.097(1)	9.033(2)
$V/Å^3$	1562.0(3)	3536(1)
Z	4	8
$D_x/g\,cm^{-3}$	1.31	1.31
λ	0.71069	0.71069
$F(000)$	656	1445
μ/cm^{-1}	2.73	2.58
Approximate crystal size/mm	$0.25 \times 0.40 \times 0.60$	$0.30 \times 0.32 \times 0.40$
Collection range, $(\sin\theta/\lambda)_{max}/Å^{-1}$	0.62	0.56
Range of hkl	$0 \leqslant h \leqslant 20$	$0 \leqslant h \leqslant 29$
	$0 < k \leqslant 12$	$0 \leqslant k \leqslant 16$
	$-11 \leqslant l \leqslant 11$	$0 \leqslant l \leqslant 10$
Indices of standard reflections	$-1\ 2\ -4$	$-1\ -3\ 2$
No. of measured reflections	3459	2741
No. of unique (R_{merge})	1645 (0.026)	2741
No. of observed reflections $[I \geqslant 2.5\sigma(I)]$	1214	1372
No. of parameters	194	412
Temperature factors of H, $U/Å^2$	0.13	0.11
R	0.080	0.057
wR	0.088	0.057
$w = 1/(\sigma^2 + gF^2)$, $g =$	0.04642	0
S	0.58	2.07
(Δ/σ)	0.21	0.74
$\Delta\rho(max, min)/eÅ^{-3}$	0.41, −0.43	0.27, −0.23

and 0.31, respectively. The O atoms labelled B were included with fixed isotropic temperature factors.

Because of the disorder and the low ratio between the number of observed reflections and the number of refined parameters in both structures, some constraints on the bond lengths have been applied. The C–O, C–C and Cl–O lengths were constrained to 1.44, 1.52 and 1.42 Å, respectively, with a target e.s.d. on the constrained bond of 0.05 Å.

Both structures were tentatively refined in *Pnam*. Indeed, for III a mirror plane passes approximately through the atoms C3, C13, C14, O9, Li and Cl at $z = 0.45$; for IV a mirror plane passes approximately at $z = -0.085$ through Li, Cl, O9, C3, Ow and all the non-hydrogen atoms of the side-arm of both A and B. The coordinates were shifted to $z = 0.25$, and both structures were refined in the centrosymmetric space group. In each case high R-values were obtained, and the ClO_4 anions could not be treated properly because in the anion the O atoms are not related by the mirror plane (for example, the distances of O18 and O19 to Li are clearly different in III, being 2.08 and 2.68 Å). Space group $Pna2_1$ was thus definitively chosen for both structures.

Discussion

The atomic parameters are given in Table 2. The coordination distances are listed in Table 3. Figures 1–3

are stereoscopic views of the complex entities, showing the numbering of the atoms.[9] The torsion angles are presented in Table 4. As a consequence of the poor crystal quality and of the thermal amplitudes of the anions, the precision of the geometry is relatively low.

In III the Li cation is tetracoordinated to the three oxygen atoms of the ether and to one oxygen (O18) of the anion. The coordination distances range from 1.82(1) to 2.06(1) Å. The cation is displaced by 0.97 Å from the plane of the three ether oxygens. As expected Li^+ is pentacoordinated in both the two independent complex entities of IV: on one side it is coordinated to the three ether oxygens, and on the other side to the side-arm oxygen and to O19 of one anion in unit A or to Ow of a water molecule in unit B (see Figs. 2 and 3). The Li–O ether distances range from 1.87 to 2.09 Å.

In IV the water molecule is hydrogen-bonded on one side to another oxygen O18 of the coordinated anion and to the other side on O19 of the non-coordinated perchlorate. The hydrogen-bonding geometry is described in Table 5.

As shown in Table 4, the conformation of the ring is similar in the three independent crown units. It is similar to that observed for LiSCN · 12-crown-3[6] and for $LiClO_4 \cdot Me_6$-12-crown-3,[5] i.e. the diamond lattice conformation.[10]

The most gratifying structural feature common to

Table 2. Atomic coordinates (×10⁴) and equivalent temperature factors (in Å²).

Atom	x	y	z	$U_{eq}{}^a$
Compound III				
O1	6041(4)	3525(5)	2900(6)	0.059(5)
C2	6463(4)	4746(7)	3095(6)	0.062(5)
C3	6279(3)	5448(5)	4495(9)	0.065(5)
C4	6548(4)	4692(6)	5850(8)	0.067(5)
O5	6057(4)	3538(5)	5981(6)	0.058(5)
C6	6450(7)	2639(8)	6997(9)	0.102(5)
C7	5942(6)	1452(9)	7004(9)	0.104(5)
C8	6166(8)	526(10)	5725(9)	0.119(5)
O9	5888(2)	1099(4)	4436(8)	0.074(5)
C10	6203(4)	523(6)	3083(9)	0.085(5)
C11	5931(7)	1333(7)	1829(8)	0.093(5)
C12	6344(4)	2735(7)	1730(7)	0.066(5)
C13	5405(3)	5863(5)	4421(10)	0.092(5)
C14	6812(5)	6713(6)	4469(10)	0.106(5)
Li15	5421(4)	2804(7)	4332(10)	0.058(5)
Cl16	3671(1)	2454(1)	4423(–)	0.060(2)
O17^b	3102(5)	3440(8)	4537(9)	0.129(5)
O18^b	4319(4)	2796(9)	5310(9)	0.132(5)
O19^b	4022(7)	2411(10)	3004(9)	0.152(5)
O20^b	3381(6)	1204(8)	4310(12)	0.268(5)
O17B^c	3644(11)	2043(13)	5817(12)	0.150
O18B^c	3608(11)	1418(12)	3348(12)	0.150
O19B^c	3020(10)	3351(12)	4104(13)	0.150
O20B^c	4348(10)	3182(12)	4023(13)	0.150
Compound IV: complex unit A				
O1	4629(5)	7080(8)	645(17)	0.052(4)
C2	4685(7)	6118(13)	475(21)	0.044(4)
C3	4389(4)	5792(7)	−846(28)	0.060(3)
C4	4604(8)	6088(12)	−2276(25)	0.063(5)
O5	4645(5)	7056(10)	−2496(16)	0.052(4)
C6	4963(11)	7431(19)	−3526(25)	0.122(8)
C7	4978(12)	8489(16)	−3596(27)	0.087(7)
C8	5252(7)	8826(15)	−2208(27)	0.078(7)
O9	4992(2)	8577(5)	−928(20)	0.055(2)
C10	5261(9)	8848(17)	385(23)	0.085(7)
C11	5017(9)	8370(14)	1669(21)	0.065(5)
C12	5010(5)	7350(12)	1726(18)	0.043(4)
C13	3820(4)	6028(8)	−732(38)	0.081(4)
O14	3739(2)	6954(5)	−808(25)	0.073(3)
C15	3215(4)	7170(10)	−709(52)	0.158(8)
C16	4430(5)	4749(7)	−981(39)	0.084(3)
O17	3862(4)	8845(7)	−1169(44)	0.188(5)
O18	3295(3)	9984(6)	−1060(29)	0.108(3)
O19	4101(7)	10229(12)	−79(30)	0.238(10)
O20	3945(8)	9877(21)	−2465(21)	0.233(10)
Cl	3812(1)	9759(2)	−1036(–)	0.064(1)
Li	4349(5)	7820(11)	−981(54)	0.049(4)
Compound IV: complex unit B				
O1	2461(7)	13321(11)	568(19)	0.064(4)
C2	2258(10)	14222(21)	507(32)	0.107(9)
C3	1937(5)	14278(8)	−853(40)	0.085(4)
C4	2218(10)	14233(13)	−2236(33)	0.094(8)
O5	2482(6)	13433(13)	−2491(18)	0.079(4)
C6	2855(9)	13315(24)	−3663(23)	0.093(8)
C7	3180(11)	12509(25)	−3511(32)	0.114(9)
C8	3488(9)	12476(18)	−2209(31)	0.098(7)
O9	3195(3)	12368(6)	−841(22)	0.076(3)
C10	3465(10)	12360(22)	601(33)	0.121(9)
C11	3067(10)	12477(22)	1744(31)	0.103(8)
C12	2847(12)	13426(21)	1565(34)	0.124(10)
C13	1495(5)	13623(9)	−774(47)	0.100(5)
O14	1660(2)	12717(5)	−909(26)	0.080(3)
C15	1285(5)	12106(11)	−613(53)	0.330(13)
C16	1719(7)	15268(11)	−879(55)	0.176(8)
Li	2409(6)	12431(13)	−899(47)	0.056(4)
O1w	2379(3)	11106(6)	−997(37)	0.111(4)
Cl	1117(1)	9542(2)	−960(12)	0.076(1)
O17	1156(8)	9576(14)	−2579(17)	0.188(7)
O18	722(4)	10155(8)	−1143(29)	0.147(5)
O19	1602(4)	9832(8)	−694(34)	0.176(6)
O20	1041(4)	8689(9)	−655(40)	0.245(7)

$^a U_{eq} = (1/3)\, \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j.$ ^{b} Occupation factor 0.69. ^{c} Occupation factor 0.31.

Table 3. Coordination distances (in Å).

Distance	III	IVA	IVB
Li–O1	1.825(10)	1.97(4)	1.87(4)
Li–O5	1.990(10)	1.94(4)	2.07(4)
Li–O9	1.906(8)	2.04(2)	2.09(2)
Li–O18	2.065(11)	—	—
Li–O14	—	2.07(2)	2.04(2)
Li–O17	—	2.00(2)	—
Li–O1w	—	—	1.95(2)

Table 4. Torsion angles (in °, σ = 2°).

Angle	III	IVA	IVB
C12–O1–C2–C3	−167	−168	163
C2–O1–C12–C11	170	169	177
O1–C2–C3–C4	66	70	−68
O1–C2–C3–C13	−65	−58	63
O1–C2–C3–C14(16)	179	−177	180
C2–C3–C4–O5	−69	−59	63
C13–C3–C4–O5	56	69	−67
C14(16)–C3–C4–O5	177	−177	177
C2–C3–C13–O14	—	67	−71
C4–C3–C13–O14	—	−62	60
C16–C3–C13–O14	—	−172	174
C3–C4–O5–C6	164	160	−168
C4–O5–C6–C7	−176	−178	165
O5–C6–C7–C8	85	72	−62
C6–C7–C8–O9	−73	−62	68
C7–C8–O9–C10	166	177	−178
C8–O9–C10–C11	−173	−167	166
O9–C10–C11–C12	71	61	−66
C10–C11–C12–O1	−72	−75	89
C3–C13–O14–C15	—	180	170

Table 5. Hydrogen bonds in IV.

A···H–D	A···D/Å	A···H/Å	A···H–D/°
O19B···H1–O1w[1]	2.804(9)	2.15(5)	154(5)
O18A···H2–O1w[2]	2.946(9)	1.77(5)	156(5)

Symmetry: [1] 0.5 − x, 0.5 + y, z − 0.5; [2] x, y, z.

ligands **III**, **IVA** and **IVB**, as well as the previously studied ligands **I** and **II**, is that they follow rather closely the predicted[10] diamond lattice conformation, not only for the ring, but also for the side-arm of **IV**. However, there was at first sight no clear feature that could explain the wide range of stabilities observed for complexes of **I**, **II** and **III**. The observed higher stability of the complex of **IV** was expected because of the additional ligating ether oxygen of the side-arm and the higher total coordination number.

Although differences in complexation constants may in part be due to differences in the solvation of the various free ligands and their complexes, such factors cannot be taken into account here, since thermochemical data are
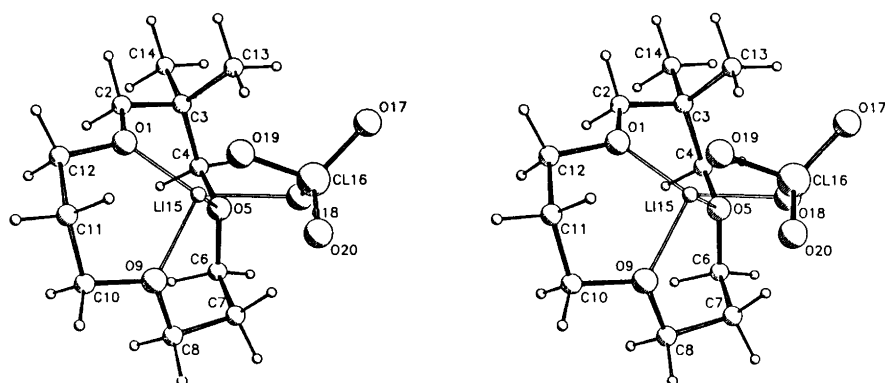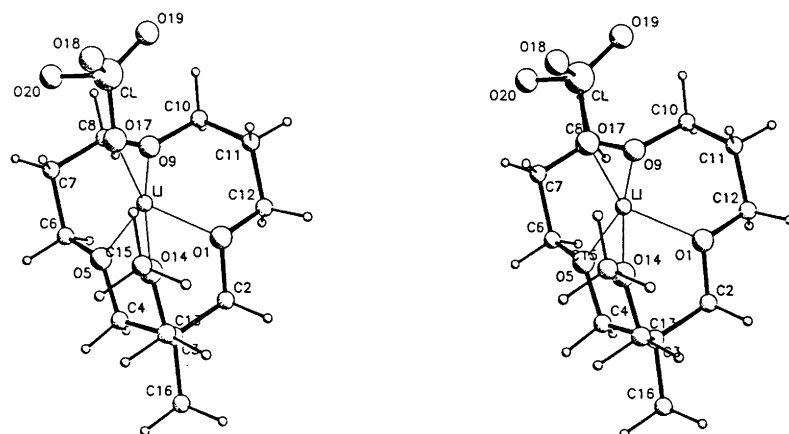
Fig. 1. Stereoscopic view of **III**.
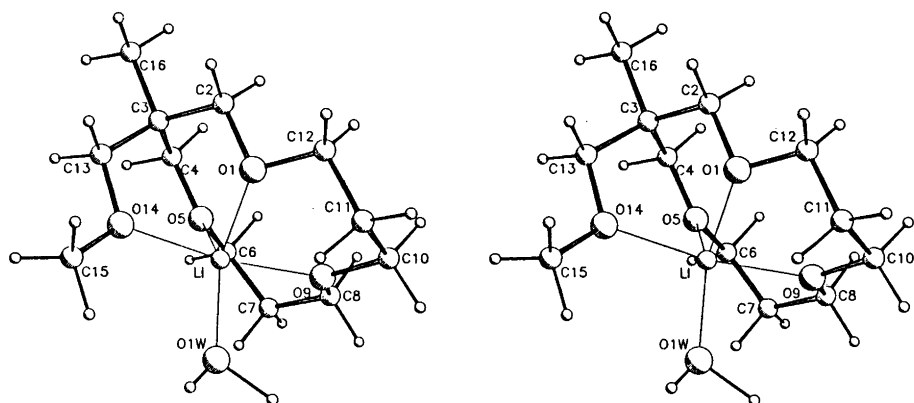

Fig. 2. Stereoscopic view of **IVA**.

Fig. 3. Stereoscopic view of **IVB**.

Table 6. Coordination distances and torsional angles in 1 : 1 complexes of 12-crown-3 ligands and lithium salts.

Ligand	Coordination no. of Li⁺	Complexation constant (log K)	H H \/ –C–C–C–	Me Me \/ –C–C–C–	–C–O–C–	Li–O (ring)	Li–O (arm)	Li–anion	Distance of Li⁺ out of O_3 plane/Å	Ref.
			Averaged ring torsion angles/°			Averaged distances to Li⁺/Å				
I	4	3.5	73	—	168	1.91	—	1.95	0.98	6
III	4	2.2	74	68	170	1.91	—	2.07	0.96	This work
II	4	0.3	—	67[a]	168[b]	1.93	—	1.96	0.97	5
IVA	5	3.9	67	65	170	1.98	2.07	2.00	1.14	This work
IVB	5	3.9	77	66	169	2.01	2.04	1.95[c]	1.20	This work

[a]62° in the free ligand. [b]155° in the free ligand. [c]H_2O instead of counter-ion.

not available. We are thus limited to an analysis based on the finer structural details for all five structures (two for **IV**) compiled in Table 6. Averaged distances from tetracoordinated Li⁺ to the ether oxygens of the ring are seen to be closely similar, and also the variation observed for the distance to the anion fails to correlate with complex stability. For pentacoordinated Li⁺, as one would expect,[11] the distances from Li⁺ to the ring oxygens are longer, and to the oxygen of the side-arm still longer, whereas the contacts to the anion, or H_2O, are much the same. The change of coordination geometry is also clearly reflected in the distance from Li⁺ to the general plane of the three ring oxygens.

The only correlation that could be established is that between complex stability and the numerical value of the averaged *gauche* torsion angles in the CC bonds of the ring (Table 6). When the β-carbon is unsubstituted, these can be adjusted without much resistance to the rather high values (ca. 73°) apparently required for good complexation, whereas smaller values (ca. 66°) are observed when the β-carbon is quaternary. However, even the attainment of these values presumably occurs at a considerable cost, since in the uncomplexed ligand **II** the averaged value is only 62°,[5] and in the related uncomplexed ligand *cis*-3,7-bis(hydroxymethyl)-3,7-dimethyl-1,5,9-trioxacyclododecane it is still smaller (55°) at quaternary carbons and much higher (66°) at unsubstituted carbon.[12]

Conclusions

In summary, we propose that it is the conformational restriction at the quaternary carbon which makes it more costly for such ligands to adjust the ring conformation to fit the size of the cation. Another manifestation of such conformational restriction has in fact been observed: oxetane and 3,3-dimethyloxetane show a very different behaviour in the BF_3-catalysed cyclotrimerization to give ligands **I** and **II**, respectively,[2] cyclization occurring more readily when no methyl substituents are present.

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