metal-organic compounds

Benzo-*cis*-cyclohexano-14-crown-4 and its lithium thiocyanate complex

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The structures of a 14-crown-4 ether containing both benzo and cyclohexano substituents, 2,6,13,17-tetraoxatricyclo-[16.4.0.0^{7,12}]docosa-1(18),19,21-triene, $C_{18}H_{26}O_4$, and its lithium complex, [2,6,13,17-tetraoxatricyclo[16.4.0.0^{7,12}]docosa-1(18),19,21-triene-κ^4O](thiocyanato-*N*)lithium(I), [Li(NCS)-($C_{18}H_{26}O_4$)], are presented. The conformation of the free crown, (I), is not preorganized for cation binding, as its donor dipoles are oriented towards opposite sides of the crown ring. The Li$^+$-crown complex, (II), exhibits two formula units in the asymmetric unit. The binding conformation observed in (II) does not completely reorient the dipoles to one point, resulting in a long Li—O bond length [2.068 (5) and 2.073 (5) Å].

Comment

Chemical substitution of the backbone of a crown-ether molecule can dramatically affect its ability to bind specific metal ions (Hay *et al.*, 1996; Sachleben *et al.*, 1996; Tobe *et al.*, 1998). As part of our investigations of the conformational changes of substitution on 14-crown-4 ether macrocycles and the effect of that substitution on the complexation of alkali metal ions (Sachleben & Moyer, 1999), we report here the structures of the free crown, (I), and its complex with lithium thiocyanate, (II).
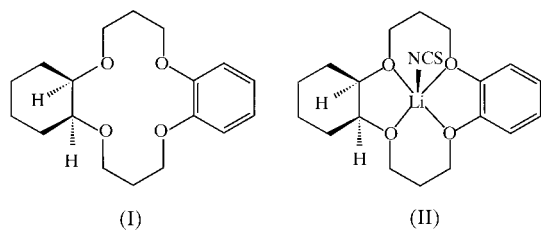
The structure of (I) is illustrated in Fig. 1. The crown conformation is quite similar to that of *cis-anti-cis*-dicyclo-hexano-14-crown-4 (Buchanan *et al.*, 1988), with pairs of O-atom dipoles oriented towards opposite sides of the crown ring. Using the convention of Dale (1980), the crown conformation can be described as $0g^-\ ag^-g^-a\ ag^+g^+\ ag^+g^+a$ (*a*),
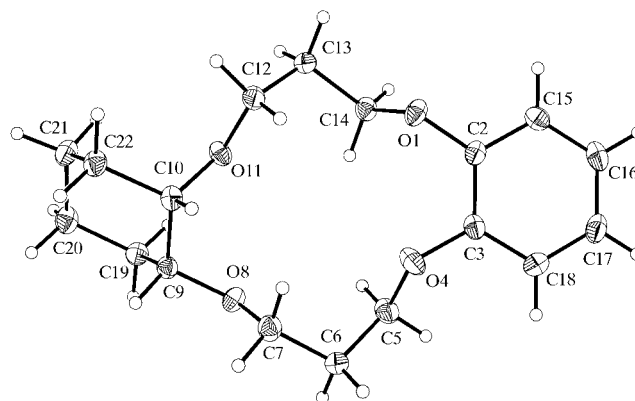

Figure 1
Molecular structure of (I) showing 50% probability displacement ellipsoids.

where 0 represents the aromatic O1—C2—C3—O4 torsion angle and spaces indicate the location of the O atoms. All bond lengths and angles are in good agreement with standard values (Allen *et al.*, 1987). For example, the Csp^3—Csp^3 bond lengths vary from 1.5114 (18) to 1.5326 (18) Å.

The structure of (II) features two formula units composing the asymmetric unit (Fig. 2). Both formula units exhibit the same overall structure with a crown conformation of $0a\ ag^+g^-a\ ag^-a\ ag^+g^-a\ a$, which allows the dipole moments of all four O atoms to be oriented towards the lithium cation. A measure of how well this is accomplished is the Ψ angle, the angle between the plane defined by any C—O—C group and the vector defined by the bond between that O atom and the cation (Hay & Rustad, 1994). All O atoms except for O4 and O8 have $\Psi < 13°$, indicating good binding to the lithium cation. The Li1—O3 and Li2—O7 bond lengths [1.972 (5) and 1.965 (5) Å] are significantly shorter than those involving an aryl ether [ranging from 2.052 (4) to 2.086 (5) Å], which is probably due to the higher basicity of the dialkyl ether. The Ψ angles for O4 and O8 are 41 and 36°, respectively, which may explain the lengthening of their Li—O bonds [2.068 (5) and 2.073 (5) Å] relative to Li1—O3 and Li2—O7.

The coordination environment of lithium in both formula units of (II) is best described as a square-based pyramid with
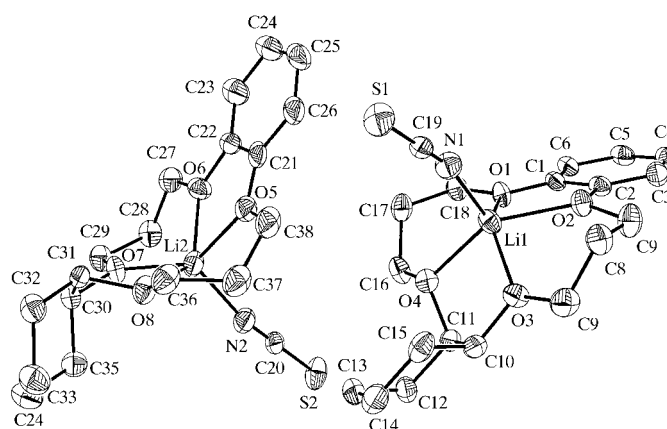

Figure 2
Molecular structure of (II) showing 50% probability displacement ellipsoids. For clarity, the H atoms have been omitted.

the thiocyanate anion occupying the apex. As calculated by *PLATON* (Spek, 1999), Li1 sits 0.729 (5) Å from a plane defined by O1–O4, and Li2 is 0.741 (5) Å from O5–O8. Again, all bond lengths and angles are in good agreement with standard values (Allen *et al.*, 1987). For example, the Csp^3—O bond lengths vary from 1.425 (3) to 1.454 (4) Å.

Experimental

Benzo-*cis*-cyclohexano-14-crown-4 was obtained as a side-product from the catalytic hydrogenation of dibenzo-14-crown-4 (Buchanan *et al.*, 1988), isolated by column chromatography, and purified by crystallization from acetone/hexanes. X-ray quality crystals were grown from an acetone solution of (I), and a 1:1 mixture of (I) and LiSCN in 1,4-dioxane for (II).

Compound (I)

Crystal data

$C_{18}H_{26}O_4$	$D_x = 1.26$ Mg m^{-3}
$M_r = 306.4$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25
$a = 9.9888$ (11) Å	reflections
$b = 15.5672$ (9) Å	$\theta = 10.1$–14.4°
$c = 10.9050$ (9) Å	$\mu = 0.088$ mm^{-1}
$\beta = 107.841$ (7)°	$T = 163$ (2) K
$V = 1614.2$ (2) Å^3	Prism, colorless
$Z = 4$	$0.43 \times 0.37 \times 0.36$ mm

Data collection

Nonius CAD-4 diffractometer	$h = 0 \rightarrow 12$
ω scans	$k = -10 \rightarrow 20$
4433 measured reflections	$l = -14 \rightarrow 13$
3677 independent reflections	3 standard reflections
2935 reflections with $I > 2\sigma(I)$	frequency: 120 min
$R_{int} = 0.021$	intensity decay: none
$\theta_{max} = 27.5°$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2$
$R(F) = 0.037$	$+ 0.4290P]$
$wR(F^2) = 0.100$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
3677 reflections	$\Delta\rho_{max} = 0.24$ e Å^{-3}
199 parameters	$\Delta\rho_{min} = -0.24$ e Å^{-3}
H-atom parameters not refined	

Compound (II)

Crystal data

[Li(NCS)(C$_{18}$H$_{26}$O$_4$)]	$D_x = 1.27$ Mg m^{-3}
$M_r = 371.4$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25
$a = 9.3885$ (8) Å	reflections
$b = 23.960$ (3) Å	$\theta = 10.1$–14.0°
$c = 17.744$ (2) Å	$\mu = 0.189$ mm^{-1}
$\beta = 102.507$ (8)°	$T = 100$ (2) K
$V = 3896.7$ (7) Å^3	Fragment, colorless
$Z = 8$	$0.55 \times 0.53 \times 0.21$ mm

Data collection

Nonius CAD-4 diffractometer	$h = -11 \rightarrow 10$
ω scans	$k = -28 \rightarrow 23$
10 705 measured reflections	$l = 0 \rightarrow 21$
6837 independent reflections	3 standard reflections
4556 reflections with $I > 2\sigma(I)$	frequency: 120 min
$R_{int} = 0.028$	intensity decay: 10%
$\theta_{max} = 25°$	

Table 1
Selected torsion angles (°) for (I).

O1—C2—C3—O4	0.43 (17)	O8—C9—C10—O11	56.26 (12)
C2—C3—O4—C5	126.08 (12)	C9—C10—O11—C12	−156.68 (9)
C3—O4—C5—C6	158.82 (10)	C10—O11—C12—C13	174.72 (9)
O4—C5—C6—C7	61.93 (14)	O11—C12—C13—C14	−69.43 (13)
C5—C6—C7—O8	66.15 (13)	C12—C13—C14—O1	−73.07 (12)
C6—C7—O8—C9	177.12 (9)	C13—C14—O1—C2	−179.30 (9)
C7—O8—C9—C10	65.24 (12)	C14—O1—C2—C3	−82.11 (13)

Table 2
Selected geometric parameters (Å, °) for (II).

O1—Li1	2.052 (4)	O7—C29	1.435 (3)
O2—Li1	2.086 (5)	O8—Li2	2.073 (5)
O3—Li1	1.972 (5)	N1—Li1	1.968 (5)
O4—Li1	2.068 (5)	N2—Li2	1.982 (6)
O5—C38	1.454 (4)		
S1—C19—N1	179.0 (3)	O1—Li1—O2	75.34 (15)
S2—C20—N2	179.3 (3)	O5—Li2—O7	141.5 (3)
O4—Li1—N1	107.0 (2)	O5—Li2—O8	89.0 (2)
O2—Li1—O3	85.21 (19)	O5—Li2—O6	75.72 (18)
O2—Li1—O4	141.7 (3)	O6—Li2—O7	85.5 (2)
O2—Li1—N1	111.0 (2)	O6—Li2—O8	133.4 (3)
O3—Li1—O4	80.20 (17)	O6—Li2—N2	108.3 (3)
O3—Li1—N1	106.59 (19)	O7—Li2—O8	79.85 (19)
O1—Li1—O3	134.2 (3)	O7—Li2—N2	109.8 (2)
O1—Li1—O4	89.99 (16)	O8—Li2—N2	118.3 (3)
O1—Li1—N1	119.0 (2)	O5—Li2—N2	107.9 (2)
O1—C1—C2—O2	−1.0 (3)	O5—C21—C22—O6	−3.3 (4)
C1—C2—O2—C7	169.1 (2)	C21—C22—O6—C27	176.8 (2)
C2—O2—C7—C8	179.6 (2)	C22—O6—C27—C28	170.7 (2)
O2—C7—C8—C9	72.9 (3)	O6—C27—C28—C29	72.7 (3)
C7—C8—C9—O3	−62.8 (3)	C27—C28—C29—O7	−60.8 (3)
C8—C9—O3—C10	−172.0 (2)	C28—C29—O7—C30	−177.9 (2)
C9—O3—C10—C11	−157.3 (2)	C29—O7—C30—C31	−149.9 (2)
O3—C10—C11—O4	−54.0 (3)	O7—C30—C31—O8	−53.0 (3)
C10—C11—O4—C16	−175.5 (2)	C30—C31—O8—C36	−173.9 (2)
C11—O4—C16—C17	−155.0 (2)	C31—O8—C36—C37	−167.1 (2)
O4—C16—C17—C18	82.2 (3)	O8—C36—C37—C38	82.8 (3)
C16—C17—C18—O1	−64.4 (3)	C36—C37—C38—O5	−59.6 (4)
C17—C18—O1—C1	177.4 (2)	C37—C38—O5—C21	166.0 (3)
C18—O1—C1—C2	177.8 (2)	C38—O5—C21—C22	−171.9 (3)

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0582P)^2$
$R(F) = 0.048$	$+ 2.7961P]$
$wR(F^2) = 0.135$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
6837 reflections	$\Delta\rho_{max} = 0.60$ e Å^{-3}
469 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}
H-atom parameters not refined	

A 1.1 mm collimator was used. Anisotropic displacement parameters were used for all non-H atoms. All H atoms were placed in calculated positions, refined using a riding model, and given an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of the atom to which they were attached. The C—H distances used depended on the type of C atom: C$_{aromatic}$—H = 0.95, C$_{secondary}$—H = 0.99 and C$_{tertiary}$—H = 1.00 Å.

For compound (I), data collection and cell refinement: *CAD*-4-*PC* (Enraf–Nonius, 1993); for compound (2), data collection and cell

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refinement: *CAD*-4-*PC* (Nonius, 1996); for both compounds, data reduction: *XCAD*4 (Harms, 1995); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1290). Services for accessing these data are described at the back of the journal.

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