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Polysulfonylamines. XCIII.† (1,2-Benzenedisulfonylimido-*O*)(1,4,7,10-tetraoxacyclododecane-κ^4O)lithium

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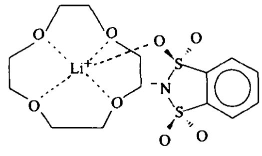
Abstract

In the title complex, [Li($C_6H_4NO_4S_2$)($C_8H_{16}O_4$)], a square-pyramidal coordination sphere around Li^+ is formed by the four mutually coplanar O atoms of 12-crown-4 at the basal positions and by one O atom of the anionic ligand, 1,3,2-benzodithiazole 1,1,3,3-tetraoxide(1−), at the apical position. The macrocycle adopts the frequently observed [3333] conformation, approximating to C_4 symmetry.

Comment

In 1:1 complexes between lithium salts Li*X* and 1,4,7,10-tetraoxacyclododecane (12-crown-4), the macrocycle commonly displays a [3333] (C_4) conformation and the metal cation is pentacoordinated by the crown O atoms at the basal positions and one donor atom of the anion X^- at the apical position of a square pyramid (Bajaj & Poonia, 1988; Power, 1988; Olsher *et al.*, 1991; for a conformational analysis of free and metal-complexed 12-crown-4, see Raithby, Shields & Allen, 1997). In contrast to the general pattern, the disulfonylamide complex [(12-crown-4)Li{N(SO_2CH_3)$_2$}], (1), exhibits a unique structure. It contains two coordination isomers, in which 12-crown-4 respectively adopts the [3333] (C_4) and the less common [48] (C_s) conformation; moreover, both Li atoms are hexacoordinated by the four ether O atoms and two geminal sulfonyl O atoms of the anion (Blaschette, Nagel & Jones, 1994). The structure determination of the title compound, (2), was prompted by these findings. Unlike (1), it surprisingly shows no new or unusual features when compared with the majority of (12-crown-4)Li*X* structures.



(2)

The asymmetric unit of (2) is shown in Fig. 1 (selected bond lengths and angles are presented in Table 1). The Li atom is coordinated by the four ether O atoms and the O1 atom of the anion in a slightly distorted square-pyramidal arrangement; the Li···O2 distance of 3.556 (4) Å is well beyond bonding distance. The O atoms of the macrocycle are coplanar within ±0.001 (1) Å, the Li atom lying 0.821 (4) Å out of this plane. The apical Li—O1 distance, 1.893 (4) Å, is 0.15–0.20 Å shorter than the basal Li—O bond lengths [average 2.087 (4) Å]. As expected, most Li—O bonds at the six-coordinate Li atoms of (1) are appreciably longer than the chemically corresponding distances in the present structure [overall averages for (1): Li—O(anion) 2.085 and Li—O(crown) 2.175 Å].

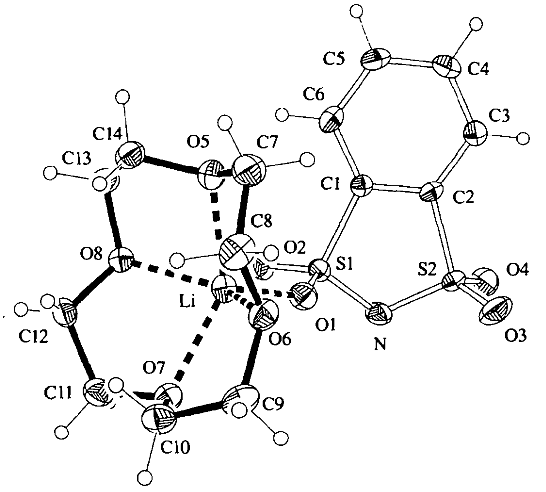


Fig. 1. The structure of the title compound in the crystal. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary.

The macrocycle in (2) shows the almost ideal C_4 symmetric [3333] conformation that is predominant in metal complexes of 12-crown-4. The C—O [average 1.437 (4) Å] and C—C distances [average 1.503 (2) Å], and the C—O—C angles [average 114.1 (2)°] are normal. The C—C—O angles are systematically larger [average 110.5 (2)°] at the C atoms C7, C9, C11 and C13 (which lie in a plane nearer to the O_4 plane) than those at the other four C atoms [average 106.2 (4)°]. Further characteristics of the [3333] conformation (Raithby, Shields & Allen, 1997) are the *gauche* O—C—C—

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† Part XCII: Henschel, Moers, Blaschette & Jones (1997).

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O torsion angles (average 54.7°) and the alternating *gauche* and *trans* C—C*n*—O—C torsion angles (average 85.6° for n = 7, 9, 11, 13; average −166.8° for n = 8, 10, 12, 14).

The geometry of the monodentate anion (Z^-) in (2) approximates to C_s symmetry and is similar to that observed in $[Ca(H_2O)_7](Z)_2$, (3), where it merely forms interionic hydrogen bonds (Moers, Blaschette & Jones, 1997). The C and S atoms are effectively coplanar, the greatest deviation from their mean plane and their mean out-of-plane distance being 0.012 (2) and 0.007 Å, respectively; N is 0.310 (2) Å out of the same plane [in (3), 0.149 (3) and 0.131 (4) Å for two independent Z^-]. The coordination to lithium induces significant deviations from C_s symmetry in the heteroatom moiety of Z^-, *e.g.* S1—O1 > S1—O2 ≃ S2—O3 ≃ S2—O4, S1—N < S2—N and O2—S1—O1 < O3—S2—O4 (*cf.* Table 1).

Experimental

1,2-Benzenedisulfonimide (HZ) was obtained as previously described (Blaschette *et al.*, 1993). Dissolving 0.50 g (2.3 mmol) of HZ and 0.10 g (2.3 mmol) of $LiOH.H_2O$ in 50 ml of deionized water, evaporating the heated solution until the onset of turbidity and storing at ambient temperature, afforded $LiZ.H_2O$ (82% yield), which was dehydrated *in vacuo* over P_4O_{10} (24 h, 353 K). To prepare complex (2), 0.51 g (1.4 mmol) of LiZ and 0.243 g (1.38 mmol) of 12-crown-4 were dissolved in 60 ml of dry methanol. The solvent was quantitatively removed *in vacuo*, the remaining solid redissolved in the minimum amount of dry acetonitrile and the solution stored at 253 K; the product crystallized in a yield of 0.39 g (71%); m.p. > 600 K. ^{1}H NMR (200 MHz, DMSO-d_6): δ 3.55 (*s*, 16H, 12-crown-4), 7.67–7.75 p.p.m. (4H, aromatic H).

Crystal data

$[Li(C_6H_4NO_4S_2)(C_8H_{16}O_4)]$
$M_r = 401.37$
Monoclinic
$P2_1/n$
$a = 8.2035 (16)$ Å
$b = 15.747 (3)$ Å
$c = 13.842 (3)$ Å
$\beta = 93.638 (16)°$
$V = 1784.5 (6)$ Å^3
$Z = 4$
$D_x = 1.494$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 50 reflections
$\theta = 10.0–11.5°$
$\mu = 0.341$ mm^{-1}
$T = 143 (2)$ K
Irregular tablet
0.60 × 0.30 × 0.15 mm
Colourless

Data collection

Stoe Stadi-4 diffractometer
ω/θ scans
Absorption correction: none
3450 measured reflections
3148 independent reflections
2666 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$

$\theta_{max} = 25.03°$
$h = -9 \rightarrow 9$
$k = -18 \rightarrow 1$
$l = -16 \rightarrow 0$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.085$
$S = 1.050$
3148 reflections
236 parameters
H-atom parameters constrained (riding)
$w = 1/[\sigma^2(F_o^2) + (0.0303P)^2 + 1.54P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.363$ e Å^{-3}
$\Delta\rho_{min} = -0.408$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0039 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Li—O1	1.893 (4)	S1—O1	1.4546 (16)
Li—O6	2.056 (4)	S1—N	1.5790 (19)
Li—O8	2.094 (4)	S2—O3	1.4381 (18)
Li—O7	2.097 (4)	S2—O4	1.4400 (18)
Li—O5	2.101 (4)	S2—N	1.5962 (19)
S1—O2	1.4377 (16)		
O1—Li—O6	109.31 (18)	O2—S1—O1	114.41 (10)
O1—Li—O8	117.2 (2)	O2—S1—N	110.86 (11)
O1—Li—O7	112.00 (19)	O1—S1—N	112.58 (10)
O6—Li—O7	81.27 (15)	O3—S2—O4	116.04 (11)
O8—Li—O7	81.32 (14)	O3—S2—N	112.75 (11)
O1—Li—O5	113.99 (19)	O4—S2—N	109.53 (10)
O6—Li—O5	81.14 (15)	S1—N—S2	114.26 (11)
O8—Li—O5	80.67 (14)	S1—O1—Li	138.58 (15)
O5—C7—C8—O6	52.7 (2)		
O6—C9—C10—O7	54.8 (2)		
O7—C11—C12—O8	55.8 (2)		
O8—C13—C14—O5	55.3 (2)		
C13—C14—O5—C7	−167.38 (18)		
C8—C7—O5—C14	85.0 (2)		
C7—C8—O6—C9	−166.96 (18)		
C10—C9—O6—C8	88.2 (2)		
C12—C11—O7—C10	84.2 (2)		
C9—C10—O7—C11	−165.85 (17)		
C11—C12—O8—C13	−166.81 (17)		
C14—C13—O8—C12	85.0 (2)		

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1354). Services for accessing these data are described at the back of the journal.

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Polysulfonylamines. XCV.† (1,2-Benzenedisulfonylimido-*N*,*O*)(1,4,7,10,13-pentaoxacyclopentadecane-κ^5O)sodium

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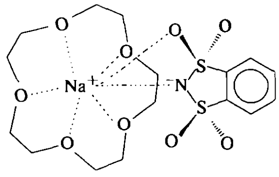
Abstract

In the title complex, $[Na(C_6H_4NO_4S_2)(C_{10}H_{20}O_5)]$, an irregular coordination sphere around Na^+ is formed by the five O atoms of 15-crown-5 and the N and one O atom of the disulfonylimide 1,3,2-benzodithiazole 1,1,3,3-tetraoxide(1−). In one C—C—O segment of the polyether ring, two successive *gauche* torsion angles of the same sign constitute a conformational corner.

Comment

The synthesis and structure determination of the title compound, (1), form part of our studies on the coordination behaviour of metal cations of Groups 1 and 2 towards di(organosulfonyl)amide anions, *e.g.* di(methanesulfonyl)amide, $(CH_3SO_2)_2N^-$ (A^-), or 1,2-benzenedisulfonylimide(1−), $C_6H_4(SO_2)_2N^-$ (Z^-). In earlier work, we reported the structures of [(15-crown-5)Na(*A*)], (2) (Blaschette, Nagel & Jones, 1993), [(12-crown-4)Li(*A*)], (3) (Blaschette, Nagel & Jones, 1994), and [(12-crown-4)Li(*Z*)], (4) (Jones, Moers & Blaschette, 1997), where 15-crown-5 is 1,4,7,10,13-pentaoxacyclopentadecane and 12-crown-4 is 1,4,7,10-tetraoxacyclododecane. Apart from the appropriate number of crown-ether O atoms, the metal is coordinated by two geminal O atoms of A^- in (3), by only one O atom of Z^- in (4), and by one O and the N atom of A^- in (2), thus attaining an overall coordination number of five in (4), six in (3) and seven in (2). The present result shows that the (15-crown-5)Na^+ fragment, in contrast to (12-crown-4)Li^+, displays essentially the same coordination behaviour towards both A^- and the bicyclic analogue Z^-.



(1)

The asymmetric unit of (1) is shown in Fig. 1 (selected geometric data are presented in Table 1). The Na^+ ion is coordinated by the five ether O atoms and the N and O1 atoms of the anion in an irregular arrangement. A major difference between structures (1) and (2) is furnished by the Na—*X*(anion) interactions. Although the bite angles O—Na—N of the anions are identical, the Na—O1 and Na—N distances in (1) are quite similar, whereas in (2), the Na—O(anion) bond length is *ca* 0.4 Å shorter than Na—N [(1): Na—O1 2.627 (3), Na—N 2.610 (3) Å and O1—Na—N 55.71 (8)°; (2): Na—O(anion) 2.349 (2), Na—N 2.758 (2) Å and O(anion)—Na—N 55.7 (1)°]. It is conceivable that the divergent coordination behaviour of A^- and Z^- in (1) and (2) and, more markedly, in (3) and (4), results from different steric demands of their respective $N(SO_2C)_2$ moiety, which approximates to C_2 symmetry in A^- and to C_s symmetry in Z^-.

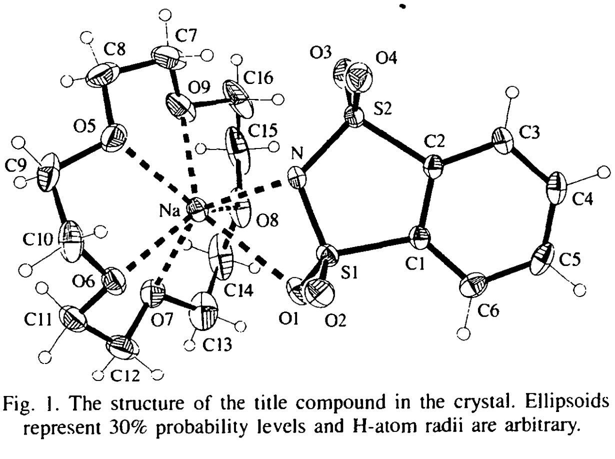


Fig. 1. The structure of the title compound in the crystal. Ellipsoids represent 30% probability levels and H-atom radii are arbitrary.

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