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Crown-Ether Complexes. IV. Lithium Nitrate Complex with Benzo-14-crown-4, $LiNO_3.C_{14}H_{20}O_4$

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Abstract. $M_r = 321{\cdot}3$, monoclinic, $P2_1/n$, $a = 14{\cdot}584$ (3), $b = 9{\cdot}074$ (3), $c = 12{\cdot}238$ (3) Å, $\beta = 91{\cdot}08$ (2)°, $V = 1619{\cdot}2$ Å^3, $Z = 4$, $D_x = 1{\cdot}32$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 10{\cdot}14$ cm^{-1}, $T = 291$ (2) K, $F(000) = 680$, $R = 8{\cdot}1\%$ for 1389 observed reflections. Li displays six coordination *via* ligation to the four O atoms of the crown-ether ring and two O atoms of an NO_3^- anion. Coordination is not octahedral, the 'bite' of the bidentate NO_3^- ligand being acute.

Introduction. The complex formed by lithium nitrate with benzo-14-crown-4 (3,4,6,7,10,11-hexahydro-2*H*,-9*H*-1,5,8,12-benzotetraoxacyclotetradecin)† might be expected to involve complexed $Li^+NO_3^-$ ion pairs (Smid, 1972). However, the infrared spectrum of Li(benzo-14-crown-4)NO_3^-, measured in the solid state (Nujol mull), shows no clear evidence of NO_3^- ion coordination (Maipass, 1980). Neither the 1384 nor the 719 cm^{-1} band of the NO_3^- ion appears as the doublet expected when the symmetry of the ion is lowered by coordination (Carter, 1976). The infrared spectrum ($CHCl_3$ solution) also fails to reveal any $Li^+NO_3^-$ interaction.

We have determined the single-crystal X-ray structure of the $LiNO_3$ complex with dibenzo-14-crown-4 to establish the nature of the bonding between the NO_3^- anion and lithium.

Experimental. The preparation of benzo-14-crown-4 has been reported (Liotta, 1980). Crystals of the complex grown from acetonitrile–toluene solutions by slow evaporation. D_m not determined. Crystal 0·03 × 0·03 × 0·02 mm. Syntex $P2_1$ automated four-circle diffractometer, room temperature, Cu $K\alpha$ radiation, θ–2θ scan mode, variable scan rate, $2\theta_{max} = 80°$, h −14 to 14, k 0 to 8, l 0 to 12. Unit-cell parameters and space-group information determined during normal alignment procedures. Three check reflections remeasured after every 97 reflections: no significant fluctuations. 2122 reflections measured; 1389 observed reflections [$I > 3\sigma(I)$] corrected for Lorentz, polarization and background effects and used in solution and refinement; no absorption correction. Computations performed using standard programs: *MULTAN*80 (Main *et al.*, 1980) and XRAY78 (Stewart, 1978). H positions located from a difference Fourier synthesis following convergence of refinement of scale factor and positional and anisotropic thermal parameters for all nonhydrogen atoms. These H positions were refined during a final series of cycles of full-matrix refinement (on F), but their temperature factors were fixed at $U = 5{\cdot}0$ Å^2. Final $R = 8{\cdot}1\%$. Unit weights used throughout, $(\Delta/\sigma)_{max} = 0{\cdot}10$. Difference-map excursions $\leq 0{\cdot}42$ e Å^{-3}. No correction for secondary extinction. Atomic scattering factors from Cromer & Mann (1968).

Discussion. A projection view of the complex is presented in Fig. 1 based on the positional parameters of Table 1.‡ Bond angles and distances are in Table 2.

Li is hexacoordinate being coordinated to the four O atoms of the crown-ether ring and to two O atoms of a bidentate NO_3^- group. Coordination is not octahedral, the 'bite' of the bidentate NO_3^- ligand being acute [O—Li—O 57·6 (1)°]. The geometry of coordination is

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† Alternative IUPAC nomenclature: 7,8,10,11,14,15-hexahydro-6*H*,13*H*-5,9,12,16-tetraoxabenzocyclotetradecene.

‡ Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38930 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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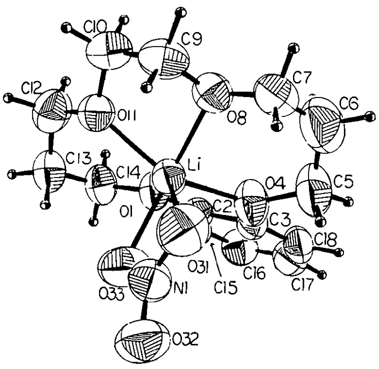

Fig. 1. Projection view of the title compound.

better perceived as square pyramidal, the four crown-ether O atoms forming the basal plane with Li displaced from that plane towards the bidentate NO_3^- ion (plane *A*; average deviation 0·24 Å) [$Li—O_{crown}$ 2·050 (4) Å]. Bonding to the nitrate is asymmetric, Li showing one longer and one shorter interaction with this ligand [$Li—O_{nitrate}$ 2·300 (4), 2·072 (4) Å]. The atoms of the nitrate group and the Li are close to coplanar with two of the crown-ether O atoms [N(1), O(31), O(32), O(33), Li(1), O(1), O(8): average deviation 0·17 Å; plane *B*] and this plane is nearly perpendicular to the plane of the crown-ether O atoms (plane *A*/plane *B* 83·5°). The firm bidentate coordination of NO_3^- suggests that the NO_3^- anion is bidentate in solution, at least in solvents of low polarity and denticity.

Four coordination is usual for Li coordinated to multiply bonded ligands. Thus lithium bromide–glycylglycine has Li tetrahedrally coordinated to four O atoms (Li—O 1·89–2·00 Å) (Meulemans, Piret & Van Meerssche, 1971) and lithium succinate shows tetrahedral coordination to four O atoms [Li—O 1·943–1·961 (2) Å] (Klapper & Küppers, 1973). Li has been observed to be five coordinate in lithium antamanide (Karle, 1974) with four carbonyl O atoms and a CH_3CN N atom ligating Li^+ (Li—O 2·12 Å), Li—O distances increasing with increasing coordination number. Another ionophore, the cryptate (211), offers six coordination sites to the encapsulated Li^+ ion with four O and two N sites [Li—O 2·081 (6)–2·173 (24) Å] in distorted octahedral array (Moras & Weiss, 1973).

The structure reported here might better be compared with the five-coordinate structures: Li(1,5,9,13-tetraoxacyclohexadecane)SCN (Groth, 1981*a*) (I) and Li(1,4,7,10-tetraoxacyclododecane)SCN (Groth, 1981*b*) (II) where the four lithium–O_{crown} distances average 2·07–2·09 Å in (I) and 2·057 (10) Å in (II). The fifth ligand in each is N; however, the $Li—O_{crown}$ distance in the 'six-coordinate' title structure is comparable to these.

The title structure with a (O—C—C—C—O—C—C—$)_2$-type ring might be viewed as intermediate in size between the (O—C—C—O—C—C—$)_2$ ring of (I) and the (O—C—C—C—O—C—C—C—$)_2$ ring of (II). Thus it is reasonable that the Li atom which is displaced 0·55 Å from the plane of the four O atoms of larger ring (II) shows greater displacement (0·85 Å) from the similar plane (plane *A*) of the smaller ring of the title structure.

Table 1. *Positional parameters and equivalent isotropic thermal parameters*

	x	*y*	*z*	U_{eq}(Å^2)*
Li(1)	0·6741 (2)	0·7120 (4)	0·9953 (3)	6·3 (2)
O(1)	0·6763 (1)	0·6344 (2)	0·8388 (1)	6·6 (1)
C(2)	0·6010 (1)	0·6654 (2)	0·7742 (2)	6·7 (1)
C(3)	0·5290 (1)	0·7429 (2)	0·8294 (2)	5·9 (1)
O(4)	0·5476 (1)	0·7615 (2)	0·9381 (1)	7·9 (1)
C(5)	0·4724 (2)	0·7973 (3)	1·0122 (2)	9·8 (2)
C(6)	0·4611 (2)	0·6915 (4)	1·0999 (2)	12·1 (2)
C(7)	0·5357 (2)	0·6720 (3)	1·1788 (2)	8·4 (2)
O(8)	0·6102 (1)	0·6015 (2)	1·1237 (1)	7·4 (1)
C(9)	0·6833 (2)	0·5651 (3)	1·1976 (2)	8·1 (2)
C(10)	0·7478 (2)	0·4683 (3)	1·1335 (2)	8·6 (2)
O(11)	0·7681 (1)	0·5525 (2)	1·0367 (1)	6·8 (1)
C(12)	0·8263)2)	0·4721 (3)	0·9628 (2)	8·8 (2)
C(13)	0·8341 (1)	0·5625 (3)	0·8584 (2)	8·2 (2)
C(14)	0·7522 (1)	0·5628 (3)	0·7848 (2)	7·7 (2)
C(15)	0·5898 (1)	0·6392 (2)	0·6649 (2)	5·3 (1)
C(16)	0·5108 (2)	0·6765 (3)	0·6089 (2)	8·2 (2)
C(17)	0·4428 (2)	0·7533 (3)	0·6620 (2)	8·6 (2)
C(18)	0·4530 (1)	0·7838 (2)	0·7728 (2)	7·4 (2)
N(1)	0·7691 (1)	0.4758 (2)	0·4661 (2)	7·2 (1)
O(31)	0·8144 (1)	0·4152 (2)	0·3930 (1)	9·9 (1)
O(32)	0·7484 (1)	0·6065 (2)	0·4629 (1)	10·3 (1)
O(33)	0·7460 (1)	0·3931 (2)	0·5430 (1)	9·9 (1)

* $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$; $\sigma(U_{eq}) = \frac{1}{2}\{[\sigma(U_{11})]^2 + [\sigma(U_{22})]^2 + [\sigma(U_{33})]^2\}^{1/2}$.

Table 2. *Bond distances* (Å) *and angles* (°)

Li(1)—O(1)	2·040 (4)	O(1)—Li(1)—O(11)	88·1 (1)
Li(1)—O(4)	2·011 (4)	O(1)—Li(1)—O(31)	146·3 (2)
Li(1)—O(8)	2·098 (4)	O(1)—Li(1)—O(4)	77·4 (1)
Li(1)—O(11)	2·051 (4)	O(1)—Li(1)—O(8)	123·6 (2)
Li(1)—O(31)	2·300 (4)	O(1)—Li(1)—O(33)	92·5 (2)
Li(1)—O(33)	2·072 (4)	O(8)—Li(1)—O(11)	77·4 (1)
		O(4)—Li(1)—O(11)	148·0 (2)
O(31)—N(1)	1·250 (3)	O(11)—Li(1)—O(31)	112·2 (2)
O(32)—N(1)	1·224 (2)	O(11)—Li(1)—O(33)	103·8 (2)
O(33)—N(1)	1·254 (3)	O(4)—Li(1)—O(8)	87·1 (1)
		O(8)—Li(1)—O(31)	88·0 (1)
O(1)—C(2)	1·371 (2)	O(8)—Li(1)—O(33)	143·8 (2)
C(2)—C(3)	1·441 (3)	O(4)—Li(1)—O(31)	94·8 (2)
C(3)—O(4)	1·363 (2)	O(4)—Li(1)—O(33)	105·1 (2)
O(4)—C(5)	1·473 (3)	O(31)—Li(1)—O(33)	57·6 (1)
C(5)—C(6)	1·452 (4)		
C(6)—C(7)	1·451 (4)	O(31—N(1)—O(32)	122·4 (2)
C(7)—O(8)	1·440 (3)	O(32)—N(1)—O(33)	122·4 (2)
O(8)—C(9)	1·423 (3)	O(31)—N(1)—O(33)	115·2 (2)
C(9)—C(10)	1·516 (3)		
C(10)—O(11)	1·446 (3)	C(2)—O(1)—C(14)	116·0 (2)
O(11)—C(12)	1·448 (3)	O(1)—C(2)—C(3)	114·4 (3)
C(12)—C(13)	1·525 (4)	C(2)—C(3)—O(4)	112·6 (2)
C(13)—C(14)	1·482 (3)	C(3)—O(4)—C(5)	119·4 (2)
O(1)—C(14)	1·454 (3)	O(4)—C(5)—C(6)	113·9 (2)
C(2)—C(15)	1·366 (3)	C(5)—C(6)—C(7)	118·5 (2)
C(15)—C(16)	1·372 (3)	C(6)—C(7)—O(8)	107·8 (2)
C(16)—C(17)	1·384 (4)	C(7)—O(8)—C(9)	111·6 (2)
C(17)—C(18)	1·388 (3)	O(8)—C(9)—C(10)	105·7 (2)
C(3)—C(18)	1·348 (3)	C(9)—C(10)—O(11)	104·9 (2)
		C(10)—O(11)—C(12)	112·2 (2)
		O(11)—C(12)—C(13)	107·8 (2)
		C(12)—C(13)—C(14)	116·0 (2)
		O(1)—C(14)—C(13)	109·6 (2)

Bond angles and distances within the crown-ether ring appear normal. The C—C distance of the O—CH_2—CH_2—O linkage, 1·516 Å, may be compared with the 1·51 (2) Å observed in (I). C—O distances of the type O—CH_2 [1·427 (3) Å] are comparable to the 1·43 (1) Å observed in (I) and (II). C—C distances in O—C—C—C—O linkages in (I) [1·478 (4) Å] are similar to the 1·51 (1) Å observed in (II).

Thus, the single-crystal X-ray structure of (benzo-14-crown-4) lithium nitrate establishes that Li is coordinated to nitrate which serves as a bidentate ligand donating two pairs of electrons to the cationic alkali metal.

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Crown-Ether Complexes. V. Lithium Nitrate Complex with a Chiral Dimethyl Derivative of Benzo-14-crown-4, $LiNO_3.C_{16}H_{24}O_4$

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Abstract. $M_r = 349{\cdot}3$, monoclinic, $P2_1$, $a = 7{\cdot}835$ (1), $b = 14{\cdot}359$ (2), $c = 8{\cdot}207$ (2) Å, $\beta = 97{\cdot}37$ (2)°, $V = 915{\cdot}7$ Å^3, $Z = 2$, $D_x = 1{\cdot}27$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$Å, $\mu = 9{\cdot}46$ cm^{-1}, $T = 291$ (2) K, $F(000) = 372$, $R = 6{\cdot}6\%$ for 1076 observed reflections. Li displays six coordination *via* ligation to the four O atoms of the crown-ether ring and two O atoms of an NO_3^- anion. Coordination is not octahedral, the 'bite' of the bidentate NO_3^- ligand being acute. The absolute configuration has been confirmed to be *R,R* at the chiral C atoms of the crown-ether ring.

Introduction. The complex formed by lithium nitrate with benzo-14-crown-4 (3,4,6,7,10,11-hexahydro-2*H*,9*H*-1,5,8,12-benzotetraoxacyclotetradecin)† (I) (Holt, Malpass, Ghirardelli, Palmer & Rubin, 1984) and with 6,7-dimethylbenzo-14-crown-4 [(6*R*,7*R*)-6,7-dimethyl-3,4,6,7,10,11-hexahydro-2*H*,9*H*-1,5,8,12-benzotetraoxacyclotetradecin] (II) (Smid, 1972) might be expected to involve complexed $Li^+NO_3^-$ ion pairs. However, the infrared spectra, measured in the solid state (Nujol mull), show no clear evidence of NO_3^- ion coordination (Malpass, 1980). Neither the 1384 nor the 719 cm^{-1} band of the NO_3^- ion appears as the doublet expected when the symmetry of the ion is lowered by coordination (Carter, 1976).

The infrared spectrum ($CHCl_3$ solution) also fails to reveal any $Li^+NO_3^-$ interaction, despite the fact that

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† Alternative IUPAC nomenclature: 7,8,10,11,14,15-hexahydro-6*H*,13*H*-5,9,12,16-tetraoxabenzocyclotetradecene.

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