

Bond angles and distances within the crown-ether ring appear normal. The C—C distance of the O—CH₂—CH₂—O linkage, 1.516 Å, may be compared with the 1.51 (2) Å observed in (I). C—O distances of the type O—CH₂ [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.

References

CARTER, R. L. (1976). *Infrared and Raman Spectroscopy. Part A*, edited by E. G. BRAME & J. G. GRASELLI. New York: Marcel Dekker.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 GROTH, P. (1981a). *Acta Chem. Scand. Ser. A*, **35**, 460–462.
 GROTH, P. (1981b). *Acta Chem. Scand. Ser. A*, **35**, 463–465.
 KARLE, I. (1974). *J. Am. Chem. Soc.* **6**, 4000–4008.
 KLAPPER, H. & KÜPPERS, H. (1973). *Acta Cryst.* **B29**, 21–26.
 LIOTTA, C. L. (1980). Private communication.
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
 MALPASS, G. D. JR (1980). PhD dissertation, Duke Univ.
 MEULEMANS, R., PIRET, P. & VAN MEERSSCHE, M. (1971). *Bull. Soc. Chim. Belg.* **80**, 73–81.
 MORAS, D. & WEISS, R. (1973). *Acta Cryst.* **B29**, 400–403.
 SMID, J. (1972). *Ions and Ion Pairs in Organic Reactions*. Vol. I, edited by M. SWARC. New York: Wiley-Interscience.
 STEWART, J. M. (1978). The XRAY system – version of 1976. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1984). **C40**, 396–398

Crown-Ether Complexes. V. Lithium Nitrate Complex with a Chiral Dimethyl Derivative of Benzo-14-crown-4, LiNO₃·C₁₆H₂₄O₄

BY ELIZABETH M. HOLT*

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, USA

G. D. MALPASS JR, R. G. GHIRARDELLI AND R. A. PALMER

Duke University, Durham, North Carolina 27706, USA

AND BYRON RUBIN

Department of Chemistry, Emory University, Atlanta, Georgia 30322, USA

(Received 11 July 1983; accepted 18 October 1983)

Abstract. $M_r = 349.3$, monoclinic, $P2_1$, $a = 7.835$ (1), $b = 14.359$ (2), $c = 8.207$ (2) Å, $\beta = 97.37$ (2)°, $V = 915.7$ Å³, $Z = 2$, $D_x = 1.27$ g cm⁻³, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 9.46$ cm⁻¹, $T = 291$ (2) K, $F(000) = 372$, $R = 6.6\%$ 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 NO₃⁻ anion. Coordination is not octahedral, the 'bite' of the bidentate NO₃⁻ 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⁺NO₃⁻ ion pairs. However, the infrared spectra, measured in the solid state (Nujol mull), show no clear evidence of NO₃⁻ ion coordination (Malpass, 1980). Neither the 1384 nor the 719 cm⁻¹ band of the NO₃⁻ ion appears as the doublet expected when the symmetry of the ion is lowered by coordination (Carter, 1976).

The infrared spectrum (CHCl₃ solution) also fails to reveal any Li⁺NO₃⁻ interaction, despite the fact that

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

* To whom correspondence should be addressed.

substantial rotational strength is observed in the NO_3^- ion $n-\pi^*$ band at 300 nm in the circular dichroism (CD) spectrum of CHCl_3 solutions of $\text{Li}(6,7\text{-dimethylbenzo-14-crown-4})\text{NO}_3$ (Liotta, 1980). Such optical activity is compelling evidence for a specific and close interaction between the NO_3^- ion and the chiral crown-ether-complexed Li^+ ion in solution.

We have determined the single-crystal X-ray structures of the LiNO_3 complex with the chiral derivative of benzo-18-crown-6 (II) to establish the nature of the bonding between the NO_3^- anion and lithium.

Experimental. The preparation of optically pure 6,7-dimethylbenzo-14-crown-4 has been reported previously (Malpass, Palmer & Ghirardelli, 1980) and is similar to the preparation of the nonmethylated compound (Liotta, 1980). Crystals of the complex (II) grown from acetonitrile-toluene solutions by slow evaporation. D_m not determined. Crystal $0.02 \times 0.03 \times 0.01$ mm. Syntex $P2_1$ automated four-circle diffractometer, room temperature, $\text{Cu } K\alpha$ radiation, $\theta-2\theta$ scan mode, variable scan rate, $2\theta_{\text{max}} = 80^\circ$, $h-13$ to 13 , $k 0$ 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. 3098 reflections measured; 1076 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: *MULTAN80* (Main *et al.*, 1980) and *XRAY78* (Stewart, 1978). Refinement of scale factor and positional and anisotropic thermal parameters for nonhydrogen atoms (only) converged to $R = 6.1\%$ in the cell of absolute configuration reported (6*R*, 7*R*), anomalous-dispersion corrections being made for O, and to $R = 6.3\%$ in the cell of opposite configuration (6*S*, 7*S*). H positions determined from a difference Fourier synthesis and included in the final cycles of refinement (on *F*) but proved unstable to refinement and thus were held constant. Unit weights. $(\Delta/\sigma)_{\text{max}} = 0.092$. Difference-map excursions $< 0.34e\text{\AA}^{-3}$. No correction for secondary extinction. Atomic scattering factors from Cromer & Mann (1968).

Discussion. A projection view is presented in Fig. 1 based on the positional parameters of Table 1.†

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,

† Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38931 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

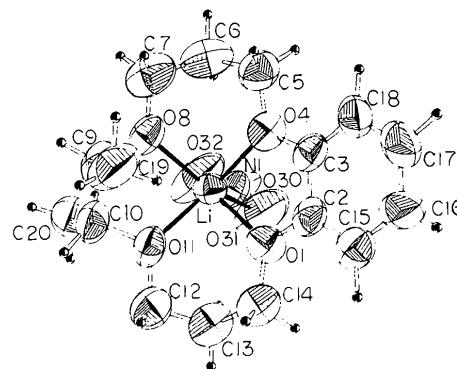


Fig. 1. Projection view of the title compound.

Table 1. Positional parameters and equivalent isotropic thermal parameters

	x	y	z	$U_{\text{eq}} (\text{\AA}^2)^*$
Li(1)	0.804 (2)	-0.964	0.371 (2)	6.6 (7)
O(1)	0.7758 (8)	-0.8312 (8)	0.2617 (8)	7.3 (7)
C(2)	0.622 (1)	-0.809 (1)	0.176 (1)	7.4 (12)
C(3)	0.497 (1)	-0.880 (1)	0.170 (1)	7.5 (12)
O(4)	0.5521 (7)	-0.9604 (9)	0.2513 (8)	7.6 (7)
C(5)	0.420 (1)	-1.026 (1)	0.273 (1)	9.7 (14)
C(6)	0.497 (1)	-1.102 (1)	0.386 (2)	10.6 (16)
C(7)	0.552 (2)	-1.072 (1)	0.561 (2)	11.7 (18)
O(8)	0.6949 (8)	-1.0138 (9)	0.5671 (7)	8.0 (8)
C(9)	0.739 (2)	-0.959 (1)	0.715 (1)	10.6 (16)
C(10)	0.920 (1)	-0.932 (1)	0.718 (1)	9.3 (15)
O(11)	0.9333 (9)	-0.8937 (9)	0.5616 (7)	8.3 (8)
C(12)	1.049 (1)	-0.816 (1)	0.565 (1)	9.7 (15)
C(13)	1.061 (1)	-0.791 (1)	0.389 (2)	9.5 (14)
C(14)	0.898 (1)	-0.756 (1)	0.292 (1)	8.9 (13)
C(15)	0.578 (1)	-0.723 (1)	0.099 (1)	8.2 (13)
C(16)	0.416 (2)	-0.710 (1)	0.018 (1)	11.1 (18)
C(17)	0.293 (2)	-0.779 (1)	0.014 (1)	10.2 (17)
C(18)	0.330 (1)	-0.864 (1)	0.087 (1)	8.8 (14)
C(19)	0.621 (2)	-0.874 (1)	0.716 (2)	14.4 (21)
C(20)	1.047 (2)	-1.014 (1)	0.747 (2)	11.6 (17)
N(1)	-0.018 (1)	-0.081 (1)	0.209 (1)	7.6 (10)
O(30)	0.0626 (9)	-0.1374 (9)	0.1414 (10)	9.9 (9)
O(31)	-0.054 (2)	-0.005 (1)	0.156 (1)	18.6 (19)
O(32)	-0.064 (2)	-0.086 (1)	0.339 (1)	21.8 (22)

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

the 'bite' of the bidentate NO_3^- ligand being acute [$51.7(6)^\circ$]. The geometry of coordination is square pyramidal, the four crown-ether O atoms forming the basal plane with Li displaced from the plane towards the bidentate NO_3^- ion (plane *A*; average deviation 0.06 \AA) [$\text{Li}-\text{O}_{\text{crown}} 2.066(14) \text{ \AA}$ average]. Bonding to the nitrate is asymmetric, each Li showing one longer and one shorter interaction with this ligand [$\text{Li}-\text{O}_{\text{nitrate}} 2.074(18), 2.286(19) \text{ \AA}$]. The firm bidentate coordination of NO_3^- suggests that the NO_3^- ion is bidentate in solution, at least in solvents of low polarity and denticity.

Four coordination is usual for Li coordinated to multiply bonded ligands, as seen in lithium bromide-glycylglycine ($\text{Li}-\text{O} 1.89-2.00 \text{ \AA}$) (Meulemans, Piret & Van Meerssche, 1971) and lithium succinate

[Li—O 1.943–1.961 (2) Å] (Klapper & Küppers, 1973) both of which show Li tetrahedrally coordinated to four O atoms. Five-coordinate Li has been observed in lithium antamanide (Karle, 1974) with four carbonyl O atoms and a CH₃CN N atom ligating Li⁺ (Li—O 2.21 Å). 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). Thus Li—O distances increase with increasing coordination number.

The five-coordinate structures Li(1,5,9,13-tetraoxacyclohexadecane)SCN (Groth, 1981*a*) (III) and Li(1,4,7,10-tetraoxacyclododecane)SCN (Groth, 1981*b*) (IV), where the four Li—O_{crow}n distances average 2.07–2.09 Å in (III) and 2.057 (10) Å in (IV) (the fifth ligand in each is N), provide better comparison to the title structure.

Bond angles and distances within the crown-ether ring appear normal. The single ethylene (O—CH₂—CH₂—O) group is dimethyl substituted and thus shorter [C—C 1.47 (2) Å]. C—O distances of the type O—CH₂ [1.41 (2) Å] are comparable to the 1.43 (1) Å observed in (III) and (IV). C—C distances in O—C—C—O linkages [1.51 (2) Å] are similar to the 1.51 (1) Å observed in (IV).

The chirality of (II) as indicated by better refinement in the *R,R* modification is exactly as expected considering the starting material and synthetic technique (Malpass, Palmer & Ghirardelli, 1980). Other spectroscopic evidence has also been given which supports the conclusion that strong ion-pair bonding between the crown-complexed Li⁺ ion and NO₃⁻ persists in solution as long as the polarity and donicity of the solvent are low. For example, the NO₃⁻ *n*-π* CD is annulled in solutions of Li(6,7-dimethylbenzo-14-crown-4)NO₃ in CF₃CH₂OH, a polar, anion-solvating solvent; whereas the CD in CH₃CN is almost as great as it is in CHCl₃, a reflection of the rather modest donicity of acetonitrile (Gurman, 1968).

Similar solution CD evidence of strong metal–nitrate ion pairing in CHCl₃, CH₂Cl₂, CH₃CN and other low-donicity solvents and solvent mixtures for LiNO₃, NaNO₃, Zn(NO₃)₂ and other metal nitrates complexed with 6,7-dimethylbenzo-14-crown-4 and its hydro-generated analog, as well as with chiral 12-crown-4, 15-crown-5 and 18-crown-6 rings has been observed. A more extensive description of this work is in preparation (Malpass & Palmer, 1984) and further structural studies are in progress (Holt, 1984).

References

- CARTER, R. L. (1976). *Infrared and Raman Spectroscopy. Part A*, edited by E. G. BRAME & J. G. GRASELLI. New York: Marcel Dekker.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- GROTH, P. (1981*a*). *Acta Chem. Scand. Ser. A*, **35**, 460–462.
- GROTH, P. (1981*b*). *Acta Chem. Scand. Ser. A*, **35**, 463–465.
- GURMAN, V. (1968). *Coordination Chemistry in Non-Aqueous Solutions*. Berlin: Springer-Verlag.
- HOLT, E. M. (1984). In preparation.
- HOLT, E. M., MALPASS, G. D., GHIRARDELLI, R. G., PALMER, R. A. & RUBIN, B. (1984). *Acta Cryst.* **C40**, 394–396.
- KARLE, I. (1974). *J. Am. Chem. Soc.* **6**, 4000–4008.
- KLAPPER, H. & KÜPPERS, H. (1973). *Acta Cryst.* **B29**, 21–26.
- LIOTTA, C. L. (1980). Private communication.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MALPASS, G. D. JR (1980). PhD dissertation, Duke Univ.
- MALPASS, G. D. JR & PALMER, R. A. (1984). In preparation.
- MALPASS, G. D. JR, PALMER, R. A. & GHIRARDELLI, R. G. (1980). *Tetrahedron Lett.* **21**(16), 1489–1492.
- MEULEMANS, R., PIRET, P. & VAN MEERSSCHE, M. (1971). *Bull. Soc. Chim. Belg.* **80**, 73–81.
- MORAS, D. & WEISS, R. (1973). *Acta Cryst.* **B29**, 400–403.
- SMID, J. (1972). *Ions and Ion Pairs in Organic Reactions*. Vol. I, edited by M. SWARC. New York: Wiley-Interscience.
- STEWART, J. M. (1978). The XRAY system—version of 1976. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1984). **C40**, 398–401

Structure and Absolute Configuration of (–)₅₈₉-[2-(Methylthio)propionato-S,O][tris(2-aminoethyl)amine]cobalt(III) Diperchlorate, [Co(C₄H₇O₂S)(C₆H₁₈N₄)](ClO₄)₂

BY S. OHBA AND Y. SAITO

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3, Kohoku-ku, Yokohama 223, Japan

(Received 19 August 1983; accepted 11 November 1983)

Abstract. *M_r* = 523.2, orthorhombic, *P*2₁2₁2₁, *a* = 11.346 (1), *b* = 15.554 (2), *c* = 11.044 (1) Å, *V* = 1949.0 (4) Å³, *Z* = 4, *D_m*(ethanol/tetrabromoethane) = 1.78 (2), *D_x* = 1.78 Mg m⁻³, *Mo Kα₁*, *λ* =

0.70926 Å, *μ* = 1.31 mm⁻¹, *F*(000) = 1080, *T* = 297 (2) K, final *R* is 0.042 for 2310 observed unique reflections. The Co atom is surrounded octahedrally by four N atoms of N(CH₂CH₂NH₂)₃ (tren) and S and O

0108-2701/84/030398-04\$01.50

© 1984 International Union of Crystallography