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# Lithium Dibenzo-14-crown-4-acetate–Ethanol (2/1)

BY RICHARD A. SACHLEBEN AND JOHN H. BURNS

*Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee* 37831, *USA*

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**Abstract.** (Dibenzo[*b*,*i*][1,4,8,11]tetraoxacyclotetradeca-2,9-dien-6-ylacetato)lithium–ethanol (2/1), [Li($C_{20}H_{21}O_6$)].0·5$C_2H_5OH$, $M_r$ = 387·36, monoclinic, $P2_1/n$, $a$ = 9·970 (4), $b$ = 9·900 (2), $c$ = 19·79 (1) Å, $\beta$ = 102·09°, $V$ = 1910 (2) Å$^3$, $Z$ = 4, $D_x$ = 1·35 g cm$^{-3}$, Mo $K\bar{\alpha}$ radiation, $\lambda$ = 0·71069 Å, $\mu$ = 0·93 cm$^{-1}$, $F(000)$ = 820, $T$ = 295 K, $R$ = 0·048 for 1608 reflections with $I > \sigma(I)$. The acetate side arm is attached to the macrocycle in a pseudo-equatorial position, and there is no intramolecular cation–anion bonding. Instead, dimers are formed by intermolecular bonding between pairs of acetate and $Li^+$ ions.

**Experimental.** The title compound was prepared by neutralization with LiOH of 2-(*sym*-dibenzo-14-crown-4)acetic acid in ethanol (Burns & Sachleben, 1990). Colorless crystals were grown from wet ethanol solution by vapor diffusion of solvent into glycerol. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\bar{\alpha}$ radiation, $\omega/2\theta$ scan technique. Cell parameters using a needle 0·05 × 0·07 × 0·20 mm by least squares on 18 reflections ($8 < \theta < 11°$), analytical absorption correction ($\mu$ = 0·93 cm$^{-1}$), transmission 0·967–0·991. 2805 reflections ($1 < \theta < 22°$) in range $0 < h < 10$, $0 < k < 10$, $-20 < l < 20$. Corrected for decline of net intensities of three reference reflections ($50\bar{3}$, 431, 326) by 2·7%. 1608 reflections with $I > \sigma(I)$, $R_{int}$ = 0·021. *MULTAN*82 and Fourier syntheses determined the structure using Enraf–Nonius *SDP* (Frenz, 1983). Carboxylate group partially disordered; ethanol is disordered over four sites in the asymmetric unit: two independent molecular orientations (Fig. 1) with the C—C bond across a center of symmetry at $\frac{1}{2},\frac{1}{2},0$ or $0,0,\frac{1}{2}$. Stoichiometry [(2/1)] dictated by this symmetry. H atoms in calculated sites, none on the ethanol. Full-matrix least-squares refinement of 281 parameters, using values of $F_o$. Anisotropic thermal parameters for all non-H atoms except C(21) and C(22). At convergence $R$ = 0·048, $wR$ = 0·056, $S$ = 1·54, $(\Delta/\sigma)_{max} < 0·01$, $(\Delta\rho)_{max}$ = 0·18, $(\Delta\rho)_{min}$ = −0·17 e Å$^{-3}$. Observations weighted as $4F_o^2/\{[\sigma(I)]^2 + (0·05F_o^2)^2\}$, where $I$ = scaled intensity and $\sigma(I)$ is based on counting statistics. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). No correction for extinction. Refined atomic parameters and equivalent isotropic thermal parameters are given in Table 1, and bond lengths and angles are in Table 2.* One dimeric unit is shown in Fig. 1.

Table 1. *Positional and equivalent isotropic thermal parameters*

$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| O(1) | 0·8104 (2) | −0·1578 (2) | 0·3431 (1) | 4·47 (6) |
| O(2) | 0·5403 (2) | −0·1446 (2) | 0·2728 (1) | 4·25 (5) |
| O(3) | 0·5024 (2) | 0·0655 (2) | 0·3398 (1) | 3·78 (5) |
| O(4) | 0·7728 (2) | 0·0548 (2) | 0·4072 (1) | 3·84 (5) |
| O(5) | 0·9489 (3) | 0·3234 (3) | 0·0639 (1) | 6·15 (7) |
| O(6*A*) | 0·3498 (5) | 0·3467 (5) | 0·5019 (3) | 6·8 (1) |
| O(6*B*) | 0·6174 (7) | 0·6248 (7) | 0·4602 (4) | 11·6 (2) |
| O(7*A*) | 0·603 (1) | 0·128 (1) | 0·0319 (7) | 6·7 (3) |
| O(7*B*) | 0·654 (1) | 0·013 (1) | 0·0631 (6) | 7·7 (3) |
| C(1) | 0·8211 (4) | −0·2762 (4) | 0·3022 (2) | 5·5 (1) |
| C(2) | 0·6823 (4) | −0·3420 (4) | 0·2844 (2) | 5·5 (1) |
| C(3) | 0·5734 (4) | −0·2614 (4) | 0·2362 (2) | 4·96 (9) |
| C(4) | 0·4349 (3) | −0·0629 (3) | 0·2398 (2) | 3·39 (7) |
| C(5) | 0·3543 (4) | −0·0862 (3) | 0·1754 (2) | 4·16 (8) |
| C(6) | 0·2489 (4) | 0·0024 (4) | 0·1490 (2) | 4·63 (9) |
| C(7) | 0·2257 (4) | 0·1124 (4) | 0·1858 (2) | 4·64 (9) |
| C(8) | 0·3086 (3) | 0·1392 (4) | 0·2502 (2) | 3·97 (8) |
| C(9) | 0·4129 (3) | 0·0508 (3) | 0·2771 (2) | 3·19 (7) |
| C(10) | 0·4924 (3) | 0·1847 (3) | 0·3796 (2) | 3·67 (8) |
| C(11) | 0·5948 (3) | 0·1758 (3) | 0·4476 (2) | 3·26 (7) |
| C(12) | 0·7433 (3) | 0·1774 (3) | 0·4399 (2) | 3·68 (8) |
| C(13) | 0·9069 (3) | 0·0302 (3) | 0·4044 (1) | 3·27 (7) |
| C(14) | 1·0169 (3) | 0·1096 (4) | 0·4341 (2) | 4·21 (8) |
| C(15) | 1·1486 (3) | 0·0726 (4) | 0·4272 (2) | 5·07 (9) |
| C(16) | 1·1683 (4) | −0·0398 (4) | 0·3906 (2) | 5·5 (1) |
| C(17) | 1·0581 (3) | −0·1195 (4) | 0·3610 (2) | 5·03 (9) |
| C(18) | 0·9276 (3) | −0·0850 (3) | 0·3689 (2) | 3·82 (8) |
| C(19) | 0·5718 (3) | 0·2952 (3) | 0·4937 (2) | 3·95 (8) |
| C(20) | 0·4505 (3) | 0·2763 (3) | 0·5278 (2) | 3·99 (8) |
| C(21) | 0·470 (1) | −0·025 (1) | −0·0373 (5) | 8·5 (3)* |
| C(22) | 0·424 (1) | −0·006 (1) | −0·0087 (6) | 10·6 (3)* |
| Li | 0·6329 (5) | −0·0935 (6) | 0·3730 (3) | 4·0 (1) |

Occupancy factors: O(6*A*), 0·546 (5); O(6*B*), 0·454; O(7*B*), 0·256 (4); O(7*A*), 0·244; C(21), 0·488; C(22), 0·512.

* These atoms have isotropic thermal parameters.

**Related literature.** Crown ethers with functionalized side arms have been studied with respect to their coordinating ability for $Na^+$ and $Li^+$ ions (Shoham, Christianson, Bartsch, Heo, Olsher & Lipscomb, 1984; Sachleben, Burns & Brown, 1988; Burns &

* Tables of structure factors, anisotropic thermal parameters and calculated H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54055 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

| | | | |
|---|---|---|---|
| Li—O1 | 2·080 (5) | C12—O4 | 1·433 (3) |
| Li—O2 | 2·067 (5) | O4—C13 | 1·373 (3) |
| Li—O3 | 2·060 (6) | C13—C14 | 1·377 (4) |
| Li—O4 | 2·041 (5) | C13—C18 | 1·377 (4) |
| Li—O5 | 1·824 (6) | C14—C15 | 1·397 (4) |
| C1—O1 | 1·441 (4) | C15—C16 | 1·364 (5) |
| C1—C2 | 1·504 (5) | C16—C17 | 1·380 (5) |
| C2—C3 | 1·513 (5) | C17—C18 | 1·385 (4) |
| C3—O2 | 1·439 (4) | C18—O1 | 1·378 (3) |
| O2—C4 | 1·377 (3) | C19—C20 | 1·515 (4) |
| C4—C5 | 1·377 (4) | C20—O5 | 1·220 (4) |
| C4—C9 | 1·388 (4) | C20—O6*A* | 1·24 (1) |
| C5—C6 | 1·384 (4) | C20—O6*B* | 1·24 (1) |
| C6—C7 | 1·358 (4) | O7*A*—C21 | 1·27 (2) |
| C7—C8 | 1·392 (4) | O7*B*—C22 | 1·19 (2) |
| C8—C9 | 1·378 (4) | C21—C'21 | 1·49 (3) |
| C9—O3 | 1·376 (3) | C22—C'22 | 1·55 (3) |
| O3—C10 | 1·433 (3) | O6*A*···O7*A* | 2·66 (2) |
| C10—C11 | 1·513 (4) | O6*A*···O7*B* | 2·87 (2) |
| C11—C12 | 1·520 (4) | O6*B*···O7*A* | 2·76 (4) |
| C11—C19 | 1·539 (4) | O6*B*···O7*B* | 2·66 (2) |

| | | | |
|---|---|---|---|
| O1—C1—C2 | 108·1 (3) | O4—C13—C14 | 125·2 (3) |
| C1—C2—C3 | 115·1 (3) | C13—C14—C15 | 119·3 (3) |
| C2—C3—O2 | 108·4 (3) | C14—C13—C18 | 120·0 (2) |
| C3—O2—C4 | 117·8 (2) | C14—C15—C16 | 120·6 (3) |
| O2—C4—C9 | 114·5 (2) | C15—C16—C17 | 120·1 (3) |
| O2—C4—C5 | 125·5 (3) | C16—C17—C18 | 119·6 (3) |
| C4—C5—C6 | 119·6 (2) | C17—C18—C13 | 120·4 (3) |
| C5—C4—C9 | 120·1 (3) | C17—C18—O1 | 125·0 (3) |
| C5—C6—C7 | 120·4 (3) | C18—O1—C1 | 118·5 (2) |
| C6—C7—C8 | 120·6 (4) | C10—C11—C19 | 109·1 (2) |
| C7—C8—C9 | 119·3 (3) | C12—C11—C19 | 108·7 (2) |
| C8—C9—C4 | 120·0 (3) | C11—C19—C20 | 113·6 (2) |
| C8—C9—O3 | 125·1 (2) | C19—C20—O5 | 118·0 (3) |
| C9—O3—C10 | 118·4 (2) | C19—C20—O6*A* | 113·5 (7) |
| O3—C10—C11 | 109·3 (2) | C19—C20—O6*B* | 120·4 (8) |
| C10—C11—C12 | 113·5 (3) | O5—C20—O6*A* | 126·0 (6) |
| C11—C12—O4 | 109·4 (2) | O5—C20—O6*B* | 117 (1) |
| C12—O4—C13 | 117·5 (2) | O7*A*—C21—C'21 | 106 (2) |
| O4—C13—C18 | 114·8 (3) | O7*B*—C22—C'22 | 120 (1) |

Primed atoms have been transformed by $1-x, -y, -z$.

Sachleben, 1990). Of special interest is whether the side arm forms *intra*molecular bonds to cations complexed by the crown, because such bonding is assumed to be present to explain the solution behavior of similar molecules (Adamic, Eyring, Petrucci & Bartsch, 1985; Dutton, Fyles & McDermid, 1988).

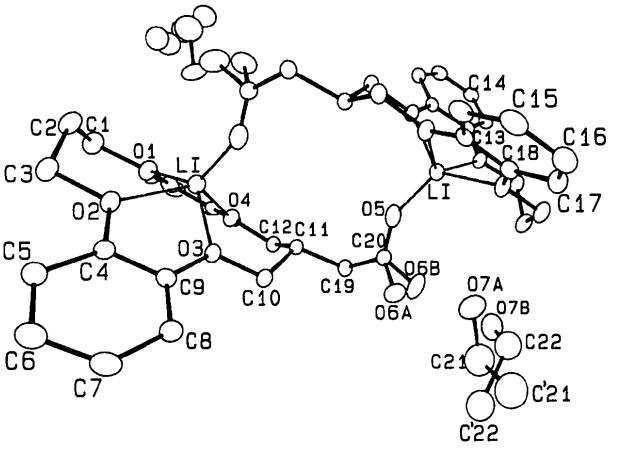


Fig. 1. One centrosymmetric dimer, 20% probability ellipsoids, numbered as in Table 1. Both sites shown for disordered ethanol.

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# Structure of Dibutanidobis(2,4,6-trimethylbenzoato)tin

BY M. F. GARBAUSKAS AND J. H. WENGROVIUS

*General Electric Corporate Research and Development, PO Box* 8, *Schenectady, NY* 12301, *USA*

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**Abstract.** $[Sn(C_4H_9)_2(C_{10}H_{11}O_2)_2]$, $M_r = 559{\cdot}3$, monoclinic, $P2_1/n$, $a = 12{\cdot}07\ (2)$, $b = 9{\cdot}976\ (10)$, $c = 22{\cdot}76\ (4)$ Å, $\beta = 91{\cdot}60\ (10)°$, $V = 2739{\cdot}5$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}356$ g cm$^{-3}$, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 9{\cdot}63$ cm$^{-1}$, $F(000) = 1160$, $T \simeq 203$ K, $R = 0{\cdot}0699$ for 2286 unique observed reflections. The title compound is monomeric with distorted octahedral coordination about the Sn atom. The four O atoms of the carboxylate groups and the central Sn atom are coplanar, with a maximum deviation out of the

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