

C27	-0.067 (1)	0.102 (1)	0.2719 (9)	0.0651
C28	-0.141 (2)	0.195 (1)	0.3130 (9)	0.0660
C29	-0.099 (1)	0.235 (1)	0.3731 (9)	0.0538
C30	0.020 (1)	0.179 (1)	0.3909 (8)	0.0525
C31	0.364 (1)	0.0314 (6)	0.2809 (9)	0.0577
C32	0.481 (1)	0.0168 (7)	0.292 (1)	0.0709
C33	0.573 (1)	0.0236 (7)	0.226 (1)	0.0702
C34	0.545 (1)	0.0455 (6)	0.146 (1)	0.0597
C35	0.427 (2)	0.0615 (7)	0.130 (1)	0.0608
C36	0.337 (1)	0.0527 (6)	0.1991 (9)	0.0619
C37	0.276 (2)	-0.116 (1)	0.3644 (7)	0.0661
C38	0.177 (2)	-0.146 (1)	0.4004 (7)	0.0707
C39	0.204 (2)	-0.251 (1)	0.4024 (7)	0.0728
C40	0.322 (2)	-0.318 (2)	0.3708 (8)	0.0902
C41	0.420 (2)	-0.291 (2)	0.3360 (8)	0.0988
C42	0.397 (2)	-0.187 (1)	0.3317 (7)	0.0921
C43	0.2532 (9)	0.058 (1)	0.470 (1)	0.0491
C44	0.2747 (8)	0.146 (1)	0.475 (1)	0.0577
C45	0.2603 (9)	0.188 (1)	0.557 (1)	0.0649
C46	0.2261 (9)	0.144 (1)	0.630 (1)	0.0810
C47	0.2062 (9)	0.058 (1)	0.622 (1)	0.0692
C48	0.2188 (8)	0.013 (1)	0.542 (1)	0.0658
C51	0.468 (2)	0.370 (2)	0.438 (1)	0.0882

Table 2. Selected geometric parameters (Å, °)

U1—Cl1	2.676 (4)	U2—Cl3	2.667 (4)
U1—Cl2	2.672 (4)	U2—Cl4	2.684 (5)
U1—O1	1.75 (1)	U2—O2	1.77 (1)
Cl1—U1—Cl2	90.1 (2)	Cl3—U2—Cl4	89.8 (1)
Cl1—U1—O1	90.8 (4)	Cl3—U2—O2	89.9 (4)

In the full-matrix least-squares refinement, a total of 632 restraints were applied to the parameters of the Ph₄P⁺ groups; each phenyl ring was restrained to planarity, P—C and C—C bond lengths were restrained to their common mean, and the *U_{ij}* parameters were restrained so that $\Delta U \approx 0$ along bond vectors. Anisotropic displacement parameters were refined for all non-H atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *CRYSTALS*. Molecular graphics: *CAMERON* (Pearce, Watkin & Prout, 1992). Software used to prepare material for publication: *CRYSTALS*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1235). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(*N,N*-dimethylformamide)(pyrocatechol-*ato-O,O'*)lithium

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Abstract

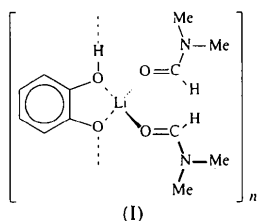
Reaction of catechol with *n*-butyllithium in absolute *n*-hexane yields the corresponding monoanion, which crystallizes from *N,N*-dimethylformamide/*n*-hexane solution as the title compound, [Li(C₆H₅O₂)(C₃H₇NO)₂]. The structure contains Li cations each coordinated by one catechol monoanion and two *N,N*-dimethylformamide molecules with nearly tetrahedral coordination geometry. The anions are connected *via* very short O···H···O hydrogen bridges to form an infinite polymeric one-dimensional structure.

Comment

o-Benzoquinone and its reduction products *o*-benzo-semiquinone and catechol (1,2-dihydroxybenzene) are

common ligands in transition metal complexes, many of which have been structurally characterized. However, the structures of pure alkali metal salts of *o*-benzosemiquinone or catechol are unknown.

As part of our studies of the structures of organo-alkali metal compounds, in which the cation coordination and possible hydrogen bonding within the anions is of particular interest, we have reacted catechol ($pK_1 = 9.4$, $pK_2 = 13.0$) with *n*-butyllithium ($pK = 44$) to generate the monoanion. Here we report the structure of a monolithium salt of catechol, (I).



In the crystal structure of (I) (Fig. 1), the anions are connected *via* intermolecular O···H···O hydrogen bridges and form an infinite polymeric structure along the *c* axis (Fig. 2). The planes of alternate anions along the chains are inclined by $44.47(3)^\circ$. The very short O···O distance of $2.435(2)$ Å, which is about 0.5 Å shorter than the sum of the van der Waals radii of two O atoms (Bondi, 1964; Nyburg & Faerman, 1985) classifies it as a very strong (Emsley, 1980; Hibbert & Emsley, 1990) and probably symmetrical hydrogen bond (Ichikawa, 1978). The O···H distance is $1.22(4)$ Å and the O···H···O angle is $174(4)^\circ$. The structure may be compared to those of [2,5-bis(trimethylsilyl)hydroquinone]bis(dimethoxyethane)sodium (Bock, Nick, Näther & Ruppert, 1995) and of several tetracyanohydroquinone anions (Vazquez, Calabrese, Dixon & Miller, 1993), which also form infinite chains con-

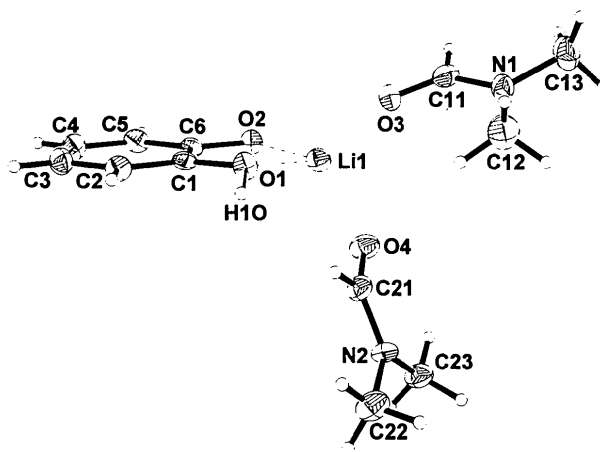


Fig. 1. View of the title compound showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level and lithium coordination as dotted lines.

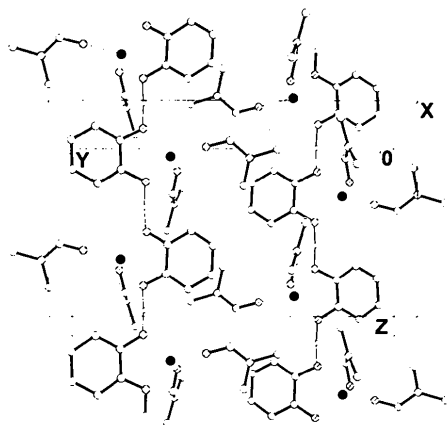


Fig. 2. The crystal structure of the title compound viewed along [100] showing the O···H···O hydrogen bridges connecting the anions. Lithium coordination is shown as dotted lines and H atoms except H10 are omitted.

ected by O···H···O hydrogen bridges, one of the latter containing the shortest intermolecular O···O distance (2.38 Å) reported so far.

The coordination sphere of the Li cation is a distorted tetrahedron with O—Li—O angles between $85.5(2)$ and $126.2(3)^\circ$. The Li—O coordination distances lie between $1.898(5)$ and $1.955(5)$ Å and correspond to standard values (Setzer & von Schleyer, 1985). The Li cation is centred between the two O atoms of the anion and shows a maximum deviation of $0.138(3)$ Å from the molecular plane. The two Li—O distances of $1.929(5)$ and $1.933(5)$ Å to the anion are nearly symmetrical and the C—O—Li angles are $110.7(2)$ and $110.5(2)^\circ$. The two C=O—Li angles to the *N,N*-dimethylformamide ligands are different: one is $121.7(2)^\circ$ and has an N—C=O—Li torsion angle of $173.5(3)^\circ$ such that the Li cation shows lone-pair directionality to the O atom of the solvent molecule, whereas the other is oriented almost in the direction of the C=O bond vector with a C=O—Li angle of $159.0(3)^\circ$.

The structure of the monoanion is an undistorted six-membered ring within experimental error and its centres deviate by less than $0.011(2)$ Å from planarity. Most of the bond distances and bond angles resemble standard values and are comparable to those of the neutral catechol molecule (Brown, 1966; Wunderlich & Mootz, 1971), except that one C—C—O angle is decreased to $115.7(2)^\circ$. All structural parameters, especially the C—O distances of $1.356(3)$ and $1.345(3)$ Å, show that the structural changes in the anion due to metallation are rather small.

Experimental

A solution of 13 ml of 15% *n*-butyllithium (20 mmol) in *n*-hexane was added to a stirred solution of 1.1 g (10 mmol) of catechol in 5 ml of absolute tetrahydrofuran at 195 K. A white precipitate formed and the reaction mixture was stirred

for 5 h at room temperature. The lithium salt was filtered off and dissolved in dry *N,N*-dimethylformamide. The resulting solution was cooled to 277 K and colourless air- and moisture-sensitive crystals grew within one week.

Crystal data

[Li(C ₆ H ₅ O ₂)(C ₃ H ₇ NO) ₂]	Mo K α radiation
$M_r = 262.23$	$\lambda = 0.71073 \text{ \AA}$
Monoclinic	Cell parameters from 30 reflections
$P2_1/c$	$\theta = 12.5\text{--}15^\circ$
$a = 8.215 (1) \text{ \AA}$	$\mu = 0.092 \text{ mm}^{-1}$
$b = 17.387 (2) \text{ \AA}$	$T = 200 (2) \text{ K}$
$c = 10.042 (1) \text{ \AA}$	Prism
$\beta = 101.92 (1)^\circ$	$0.5 \times 0.3 \times 0.3 \text{ mm}$
$V = 1403.5 (3) \text{ \AA}^3$	Colourless
$Z = 4$	
$D_x = 1.241 \text{ Mg m}^{-3}$	

Data collection

Stoe AED-II four circle diffractometer	$R_{\text{int}} = 0.064$
ω - θ scans	$\theta_{\text{max}} = 22.49^\circ$
Absorption correction: none	$h = 0 \rightarrow 8$
3691 measured reflections	$k = -18 \rightarrow 18$
1800 independent reflections	$l = -10 \rightarrow 10$
1100 observed reflections	4 standard reflections
$[I > 2\sigma(I)]$	frequency: 120 min
	intensity decay: negligible

Refinement

Refinement on F^2	Extinction correction: <i>SHELXL93</i> (Sheldrick, 1993)
$R[F^2 > 2\sigma(F^2)] = 0.0453$	Extinction coefficient: 0.0059 (13)
$wR(F^2) = 0.0894$	Atomic scattering factors from <i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
$S = 0.974$	
1800 reflections	
181 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.0348P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{\text{max}} < 0.001$	
$\Delta\rho_{\text{max}} = 0.167 \text{ e \AA}^{-3}$	
$\Delta\rho_{\text{min}} = -0.169 \text{ e \AA}^{-3}$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Li1	0.6305 (6)	0.6787 (3)	0.1758 (4)	0.0236 (11)
O1	0.7312 (2)	0.74629 (10)	0.3227 (2)	0.0220 (5)
O2	0.6960 (2)	0.75497 (10)	0.0576 (2)	0.0205 (5)
C1	0.7800 (3)	0.8130 (2)	0.2731 (2)	0.0182 (7)
C2	0.8442 (4)	0.8749 (2)	0.3531 (3)	0.0230 (7)
C3	0.8943 (4)	0.9414 (2)	0.2946 (3)	0.0281 (8)
C4	0.8780 (3)	0.9452 (2)	0.1536 (3)	0.0275 (7)
C5	0.8117 (4)	0.8834 (2)	0.0727 (3)	0.0234 (7)
C6	0.7617 (3)	0.8167 (2)	0.1297 (2)	0.0175 (6)
O3	0.6983 (2)	0.57675 (11)	0.1471 (2)	0.0346 (6)
N1	0.6328 (3)	0.45314 (13)	0.1847 (2)	0.0258 (6)
C11	0.6871 (4)	0.5086 (2)	0.1147 (3)	0.0278 (8)
C12	0.5808 (4)	0.4699 (2)	0.3119 (3)	0.0403 (9)
C13	0.6398 (4)	0.3729 (2)	0.1454 (3)	0.0382 (9)
O4	0.4030 (2)	0.66490 (11)	0.2018 (2)	0.0308 (6)
N2	0.2112 (3)	0.67814 (13)	0.3345 (2)	0.0224 (6)
C21	0.3639 (4)	0.6792 (2)	0.3121 (3)	0.0264 (7)
C22	0.1743 (4)	0.7013 (2)	0.4649 (3)	0.0342 (8)
C23	0.0712 (3)	0.6597 (2)	0.2252 (3)	0.0297 (8)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Li1—O3	1.898 (5)	C1—C2	1.380 (4)
Li1—O2	1.929 (5)	C1—C6	1.418 (3)
Li1—O1	1.933 (5)	C2—C3	1.397 (4)
Li1—O4	1.955 (5)	C3—C4	1.396 (4)
O1—C1	1.356 (3)	C4—C5	1.388 (4)
O2—C6	1.345 (3)	C5—C6	1.392 (4)
O3—Li1—O2	114.9 (2)	C2—C1—C6	120.2 (2)
O3—Li1—O1	126.2 (3)	C1—C2—C3	120.7 (2)
O2—Li1—O1	85.5 (2)	C4—C3—C2	119.4 (3)
O3—Li1—O4	103.0 (2)	C5—C4—C3	120.1 (3)
O2—Li1—O4	124.2 (3)	C4—C5—C6	121.1 (2)
O1—Li1—O4	104.1 (2)	O2—C6—C5	124.3 (2)
C1—O1—Li1	110.7 (2)	O2—C6—C1	117.2 (2)
C6—O2—Li1	110.4 (2)	C5—C6—C1	118.5 (2)
O1—C1—C2	124.1 (2)	C11—O3—Li1	159.0 (3)
O1—C1—C6	115.7 (2)	C21—O4—Li1	121.7 (2)

Data were corrected for Lorentz and polarization effects. The C, O, N and Li atoms were refined with anisotropic displacement parameters. The H atoms were located from a difference map, but placed in ideal positions and refined with individual isotropic displacement parameters using a riding model [$U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C}_{\text{aromatic}})$ or $U_{\text{iso}} = U_{\text{eq}}(\text{C}_{\text{methyl}})$]. The coordinates and an isotropic displacement parameter for the H atom of the hydroxy group were refined freely.

Data collection: *DIF4* (Stoe & Cie, 1988). Cell refinement: *DIF4*. Data reduction: *DIF4*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC XP* (Sheldrick, 1992). Software used to prepare material for publication: *SHELXL93 CIFTAB*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving non-H atoms, and torsion angles have been deposited with the IUCr (Reference: KH1058). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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