

Lithium hydrogen (*RS*)-phenylsuccinate

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Key indicators

Single-crystal X-ray study
 $T = 200$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
Disorder in main residue
 R factor = 0.050
 wR factor = 0.130
Data-to-parameter ratio = 10.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

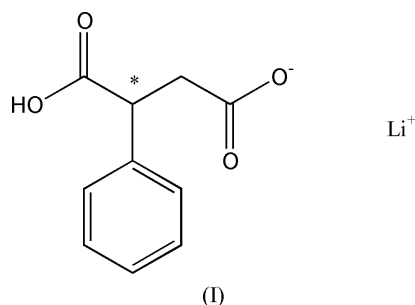
From a solution of lithium hydroxide and (*RS*)-phenylsuccinic acid in water, crystals of the title compound, $\text{Li}^+\cdot\text{C}_{10}\text{H}_9\text{O}_4^-$, were obtained. The basic structural feature is an approximately square-planar centrosymmetric Li_2O_2 unit. The Li atoms in this unit are coordinated by further O atoms, yielding a distorted tetrahedral geometry around Li.

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Comment

Carboxylic acids exhibit a fascinating wealth of structures, due to the ability of the acid molecules to form different hydrogen bonds. Possible acceptor atoms are the O atom of another carboxyl group or other acceptors with lone pairs, such as the O atoms of OH groups. Despite this variability, the structural chemistry of many simple carboxylic acids and their salts has not been explored thoroughly. This is particularly true of some technologically important acids, such as mandelic acid and phenylsuccinic acid.

Recently, we determined the structures of both (*S*)- (Fischer & Profir, 2003*a*) and (*RS*)-phenylsuccinic acid (Fischer & Profir, 2003*b*). The structural chemistry of the salts of this acid is essentially uninvestigated and we decided to prepare some salts of both the racemate and the pure enantiomer. The structure of the lithium hydrogen salt of (*RS*)-phenylsuccinic acid, (I), is presented here.



The structure of (I) contains one $\text{LiH}(\text{RS})$ -phenylsuccinate unit in the asymmetric unit (Fig. 1). The geometry of the hydrogen (*RS*)-phenylsuccinate anion is unexceptional. The Li^+ cation is located close to an inversion centre. Coordination by one carboxyl O atom thus yields a centrosymmetric $\text{Li}-\text{O}-\text{Li}-\text{O}$ unit (Fig. 2), where each Li^+ cation is coordinated by two (symmetry-equivalent) bridging acid molecules. The $\text{Li}\cdots\text{Li}^{\text{iv}}$ separation is 2.766 (9) Å (see Table 1 for symmetry code). The coordination sphere is completed by two O atoms from two other carboxyl groups, yielding a distorted tetrahedral coordination around Li^+ . The bond lengths are in the range 1.885 (5)–2.006 (4) Å and the O–Li–O angles deviate

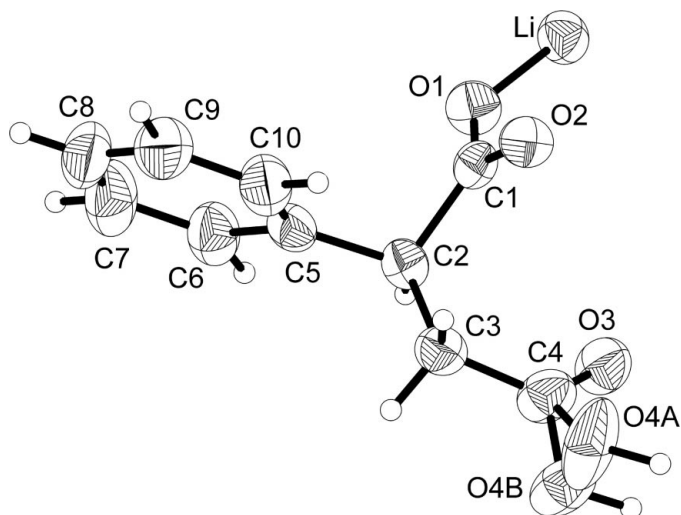


Figure 1

The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 70% probability level and H atoms are shown as small spheres of arbitrary radii. Both disorder components are shown.

significantly from the ideal tetrahedral angle [O–Li–O 91.01 (19)–121.2 (2)°]. An extended sheet structure propagating in the (100) plane arises from this connectivity, and O–H···O hydrogen bonds (Table 2) help to stabilize this arrangement.

There are a wealth of structures where Li is four-coordinated by oxygen. However, many of these compounds involve ligands such as diethyl ether and tetrahydrofuran. The number of lithium carboxylates, where Li is coordinated only by the O atoms of different carboxy groups, is much smaller. Nevertheless, there are a number of different structures that can be compared with that of (I) and a few examples exemplifying different Li geometries are distorted tetrahedral [bis(μ_2 -citrate)aqualithiumantimony dihydrate (Smith *et al.*, 1993); lithium succinate (Klapper & Küppers, 1973)], square-pyramidal [bis(μ_2 -dihydrogen DL-malato-*O,O',O''*)-bis(trihydrogen DL-malato-*O,O'*)dilithium (Fleck *et al.*, (2001)), distorted trigonal-pyramidal {catena-[diaquabis(μ_3 -citrate-*O,O'*)dilithium] (Tobon-Zapata *et al.*, 1998); lithium hydrogen malate (Kirfel *et al.*, 1983)} and distorted octahedral {catena-[μ_2 -aqua- μ_2 -(+)-tartrato-*O,O',O'',O'''*]- μ_2 -tartrato-*O,O',O''*-aquadilithium] (Bott *et al.*, 1994)}. In some structures, crystallographically independent Li⁺ cations with different coordination geometries are present. This is the case in dilithium malonate (Soriano-Garcia & Rao, 1983), where one Li atom possesses a distorted tetrahedral coordination, while the other Li atom has a strongly distorted trigonal-bipyramidal environment. Apparently, the coordination geometry around the Li atom in this type of compound depends strongly on the stereochemistry of the acid.

Experimental

A 1 M LiOH solution was prepared by dissolving anhydrous lithium hydroxide (Alfa Aesar, 98%) in demineralized water. A quantity of this solution (1 ml) was further diluted with demineralized water

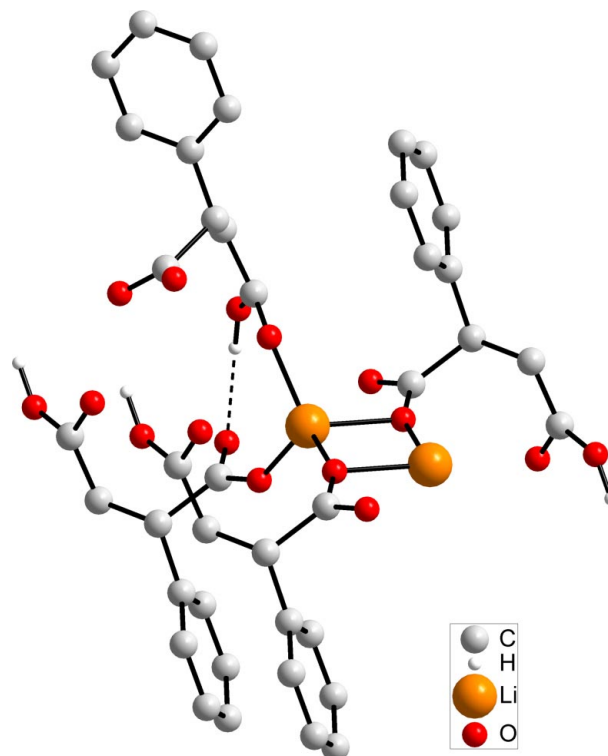


Figure 2

Detail of (I), showing the Li–O–Li–O unit. H atoms attached to C atoms have been omitted. The dashed line indicates a hydrogen bond.

(9 ml). To this solution, (*RS*)-phenylsuccinic acid (0.001 mol; Aldrich, 99%) was added. The solution was then poured into a small beaker which was placed in a desiccator over potassium hydroxide. After a couple of days, the solution had evaporated, leaving crystals of (I) in almost quantitative yield.

Crystal data

Li⁺·C₁₀H₉O₄[−]
M_r = 200.12
 Monoclinic, *P*2₁/*c*
a = 14.350 (4) Å
b = 5.3060 (9) Å
c = 12.672 (5) Å
 β = 109.96 (2)°
V = 906.9 (5) Å³
Z = 4

D_x = 1.466 Mg m^{−3}
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 5.2–16.0°
 μ = 0.11 mm^{−1}
T = 200 K
 Irregular fragment, colourless
 0.20 × 0.10 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 6944 measured reflections
 1533 independent reflections
 1130 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.086
 θ_{max} = 24.7°
h = −16 → 16
k = −4 → 6
l = −14 → 14

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.050
wR(*F*²) = 0.130
S = 1.07
 1533 reflections
 145 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 0.5204P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$

Table 1
Selected geometric parameters (Å, °).

Li–O1	1.881 (5)	Li–O2 ⁱⁱⁱ	2.006 (4)
Li–O3 ⁱ	1.940 (4)	Li···Li ^{iv}	2.776 (9)
Li–O2 ⁱⁱ	1.954 (5)		
O1–Li–O3 ⁱ	109.9 (2)	O3 ⁱ –Li–O2 ⁱⁱⁱ	108.7 (2)
O1–Li–O2 ⁱⁱ	114.0 (2)	O2 ⁱⁱ –Li–O2 ⁱⁱⁱ	91.01 (19)
O3 ⁱ –Li–O2 ⁱⁱ	121.2 (2)	Li ^v –O2–Li ⁱⁱⁱ	88.99 (19)
O1–Li–O2 ⁱⁱⁱ	109.9 (2)		

Symmetry codes: (i) $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x, y + 1, z$; (iii) $-x + 2, -y, -z + 1$; (iv) $-x + 2, -y + 1, -z + 1$; (v) $x, y - 1, z$.

Table 2
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4a–H4a···O2 ^{vi}	0.98	1.98	2.918 (4)	160
O4b–H4b···O1 ^{vii}	0.95	1.86	2.686 (4)	145

Symmetry codes: (vi) $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$; (vii) $x, -y - \frac{1}{2}, z - \frac{1}{2}$.

All H atoms were located in a difference Fourier map and were refined using a riding model in their as-found relative positions, with C–H distances in the range 0.88–1.11 Å, and with the constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$ applied in all cases. For atom O4, a structure model with a split position was applied [site occupancy factors: 0.35 for atom O4A and 0.65 for atom O4B].

Data collection: COLLECT (Nonius, 1999); cell refinement: DIRAX/LSQ (Duisenberg, 1992); data reduction: EVALCCD

(Duisenberg *et al.*, 2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg, 2001); software used to prepare material for publication: maXus (Mackay *et al.*, 1999).

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