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## Lithium and Caesium Hydrogen Glutarate

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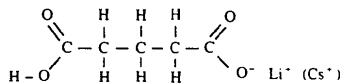
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### Abstract

In both structures, hydrogen glutarate [HO<sub>2</sub>C(CH<sub>2</sub>)<sub>3</sub>-CO<sub>2</sub>]<sup>-</sup> anions are linked into infinite chains by asymmetric O—H...O hydrogen bonds [O...O 2.614 (1) Å (Li), 2.452 (4) Å (Cs)]. The Cs salt additionally contains chains where anions are linked by symmetrical O...H...O hydrogen bonds [O...O 2.444 (4) Å]. The Li<sup>+</sup> ion is four-coordinate while both independent Cs<sup>+</sup> ions are eight-coordinate.

### Comment

The structures of lithium (I) and caesium (II) hydrogen glutarate complete our study of the alkali metal acid glutarates (see Macdonald, Morrison, Murray & Freer, 1991). Caesium hydrogen glutarate was the first such acid salt to be investigated (Macdonald, 1968) but the complexity of the Patterson function meant that its structure was not elucidated until recently. The structure of lithium hydrogen glutarate (Fig. 1) is that of a typical type *B*<sub>2</sub> acid salt, while that of the caesium salt (Fig. 2) is of a novel type.



Dibasic acid salt structures invariably contain infinitely extended chains of hydrogen-bonded acid residues. In caesium hydrogen glutarate (II), chains of glutarate anions run parallel to the *y* axis (Fig. 2). Each glutarate anion has its central C atom lying on a mirror plane and the chains are constructed from three independent anions, each with mirror symmetry. There are two types of chain: one type has the glutarate half-acid anions linked by very short hydrogen bonds [O(1)...O(1') 2.444 (4) Å] across symmetry centres and is typical of those found in type *A*<sub>2</sub> structures (Sime, Speakman & Parthasarathy, 1970); in the other chains the hydrogen bonds are formally asymmetric with O(4)...O(6)

2.452 (4) Å. This acid salt is thus unusual in that both types of hydrogen bond appear in the one structure. Moreover, the two types of hydrogen bond are both very short and are not significantly different in length.

Glutarate chains are cross-linked through electrostatic contacts to the Cs<sup>+</sup> ions. One Cs<sup>+</sup> ion lies on a twofold axis while the other is in a general position. Each ion is eight-coordinate with Cs<sup>+</sup>...O distances in the range 3.097 (3)–3.207 (4) Å for Cs(1) and 3.043 (4)–3.213 (3) Å for Cs(2).

In the lithium salt, half-acid anions are linked into infinite chains by longer [O...O 2.614 (1) Å] asymmetric hydrogen bonds (Fig. 1). The Li<sup>+</sup> ions are four-coordinate with Li<sup>+</sup>...O distances in the range 1.894 (3)–1.956 (3) Å.

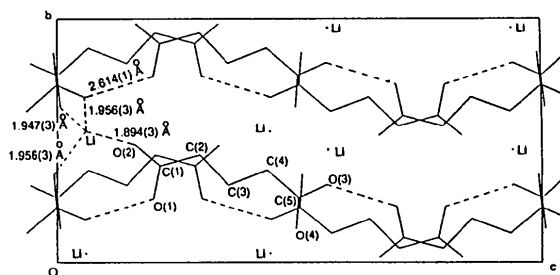


Fig. 1. Unit-cell contents of lithium hydrogen glutarate (I) viewed along *a*, showing hydrogen bonding, the Li<sup>+</sup>...O contacts to one Li<sup>+</sup> ion and the atom-numbering scheme.

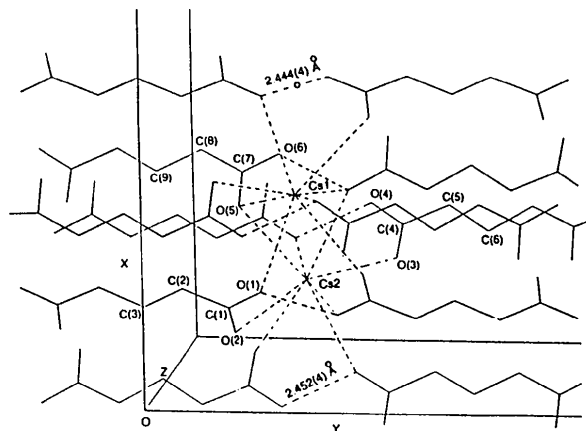


Fig. 2. Part of the structure of caesium hydrogen glutarate (II) showing the eightfold coordination around each Cs<sup>+</sup> ion, hydrogen bonding and the atom-numbering scheme.

### Experimental

Dissolving glutaric acid/lithium carbonate (1 mol:0.5 mol) for (I) and glutaric acid/caesium carbonate (1 mol:0.5 mol) for (II) in water, yielded crystals on standing.

**Compound (I)***Crystal data*

Li<sup>+</sup>.C<sub>5</sub>H<sub>7</sub>O<sub>4</sub><sup>-</sup>  
*M<sub>r</sub>* = 138  
 Orthorhombic  
*Pbca*  
*a* = 7.950 (1) Å  
*b* = 8.880 (1) Å  
*c* = 17.525 (3) Å  
*V* = 1237.2 (1) Å<sup>3</sup>  
*Z* = 8  
*D<sub>x</sub>* = 1.487 Mg m<sup>-3</sup>

*Data collection*

Enraf–Nonius CAD-4  
 diffractometer  
*ω*/*2θ* scans  
 Absorption correction:  
 none  
 1270 measured reflections  
 1270 independent reflections  
 1030 observed reflections  
 [*I* > 3σ(*I*)]

*Refinement*

Refinement on *F*  
*R* = 0.037  
*wR* = 0.051  
*S* = 2.74  
 1030 reflections  
 120 parameters  
 All H-atom parameters  
 refined  
*w* = 1/σ<sup>2</sup>(*F<sub>o</sub>*)  
 (Δ/σ)<sub>max</sub> = 0.27

**Compound (II)***Crystal data*

Cs<sup>+</sup>.C<sub>5</sub>H<sub>7</sub>O<sub>4</sub><sup>-</sup>  
*M<sub>r</sub>* = 263.8  
 Monoclinic  
*C2/m*  
*a* = 13.222 (2) Å  
*b* = 18.633 (3) Å  
*c* = 10.092 (2) Å  
*β* = 103.02 (1)°  
*V* = 2422.6 (1) Å<sup>3</sup>  
*Z* = 12  
*D<sub>x</sub>* = 1.815 Mg m<sup>-3</sup>

*Data collection*

Enraf–Nonius CAD-4  
 diffractometer  
*ω*/*2θ* scans  
 Absorption correction:  
 refined from Δ*F*  
 (DIFABS; Walker &  
 Stuart, 1983)  
 2452 measured reflections  
 2452 independent reflections

Cu Kα radiation  
*λ* = 1.5418 Å  
 Cell parameters from 25  
 reflections  
*θ* = 20–25°  
*μ* = 1.037 mm<sup>-1</sup>  
*T* = 295 K  
 Thin irregular plate  
 0.6 × 0.3 × 0.1 mm  
 Colourless

*θ*<sub>max</sub> = 75°  
*h* = 0 → 9  
*k* = 0 → 11  
*l* = 0 → 21  
 2 standard reflections  
 monitored every 200  
 reflections  
 intensity decay: <3%

Δ*ρ*<sub>max</sub> = 0.22 e Å<sup>-3</sup>  
 Δ*ρ*<sub>min</sub> = -0.16 e Å<sup>-3</sup>  
 Extinction correction:  
 Larson (1970)  
 Extinction coefficient:  
 1.79 × 10<sup>3</sup>  
 Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallography*  
 (1974, Vol. IV)

*Refinement*

Refinement on *F*  
*R* = 0.029  
*wR* = 0.043  
*S* = 2.4  
 2116 reflections  
 141 parameters  
 H-atom parameters not  
 refined  
*w* = 1/σ<sup>2</sup>(*F<sub>o</sub>*)

(Δ/σ)<sub>max</sub> = 0.35  
 Δ*ρ*<sub>max</sub> = 0.73 e Å<sup>-3</sup>  
 Δ*ρ*<sub>min</sub> = -1.35 e Å<sup>-3</sup>  
 Extinction correction: none  
 Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallography*  
 (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for (I)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
Li	0.40008 (30)	0.53812 (30)	0.06034 (10)	0.028
O(1)	0.30932 (19)	0.26594 (14)	0.19983 (6)	0.046
O(2)	0.42606 (17)	0.48019 (14)	0.16368 (6)	0.042
O(3)	0.28537 (14)	0.31978 (12)	0.55740 (5)	0.031
O(4)	0.41483 (14)	0.13751 (11)	0.49325 (5)	0.029
C(1)	0.37677 (20)	0.39674 (20)	0.21365 (10)	0.029
C(2)	0.38816 (18)	0.44069 (16)	0.29603 (8)	0.027
C(3)	0.35730 (20)	0.31830 (20)	0.35497 (10)	0.032
C(4)	0.39193 (20)	0.37922 (20)	0.43428 (10)	0.031
C(5)	0.36120 (17)	0.26965 (15)	0.49910 (7)	0.024

Table 2. Selected geometric parameters (Å, °) for (I)

O(2)—C(1)	1.212 (2)	O(1)—C(1)	1.302 (2)
C(1)—C(2)	1.498 (2)	C(2)—C(3)	1.519 (3)
C(3)—C(4)	1.517 (3)	C(4)—C(5)	1.516 (2)
C(5)—O(3)	1.264 (2)	C(5)—O(4)	1.253 (2)
O(2)—C(1)—O(1)	123.0 (2)	C(1)—C(2)—C(3)	117.3 (2)
O(1)—C(1)—C(2)	115.9 (2)	C(3)—C(4)—C(5)	115.4 (2)
C(2)—C(3)—C(4)	109.8 (2)	C(4)—C(5)—O(4)	119.0 (2)
C(4)—C(5)—O(3)	117.2 (2)	O(3)—C(5)—O(4)	123.8 (1)
O(2)—C(1)—C(2)	121.2 (2)		

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for (II)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
Cs(1)	1/2	0.24715 (2)	0	0.040
Cs(2)	0.30494 (2)	0.23486 (2)	0.32885 (2)	0.042
O(1)	0.2738 (2)	0.1926 (1)	-0.0434 (3)	0.045
O(2)	0.1816 (2)	0.1397 (1)	0.0865 (3)	0.051
O(3)	0.3593 (2)	0.3597 (2)	0.5533 (3)	0.051
O(4)	0.4857 (2)	0.3075 (1)	0.7045 (3)	0.041
O(5)	0.4728 (3)	0.1378 (2)	0.2347 (3)	0.054
O(6)	0.5981 (2)	0.1935 (1)	0.3783 (3)	0.049
C(1)	0.2383 (3)	0.1365 (2)	0.0090 (4)	0.036
C(2)	0.2786 (4)	0.0668 (2)	-0.0337 (5)	0.047
C(3)	0.2367 (5)	0.0000 (2)	0.0180 (7)	0.050
C(4)	0.4365 (3)	0.3632 (2)	0.6441 (4)	0.036
C(5)	0.4824 (4)	0.4331 (2)	0.7031 (5)	0.046
C(6)	0.4242 (5)	0.5000 (2)	0.6462 (7)	0.044
C(7)	0.5519 (3)	0.1367 (2)	0.3246 (4)	0.036
C(8)	0.6023 (3)	0.0672 (2)	0.3808 (5)	0.042
C(9)	0.5507 (5)	0	0.3141 (6)	0.042

Table 4. Selected geometric parameters (Å, °) for (II)

O(1)—C(1)	1.305 (5)	C(1)—C(2)	1.502 (6)
O(2)—C(1)	1.202 (6)	C(2)—C(3)	1.503 (6)
O(3)—C(4)	1.210 (6)	C(4)—C(5)	1.501 (6)
O(4)—C(4)	1.302 (5)	C(5)—C(6)	1.509 (6)
O(5)—C(7)	1.221 (5)	C(7)—C(8)	1.507 (6)
O(6)—C(7)	1.280 (5)	C(8)—C(9)	1.510 (6)
O(1)—C(1)—O(2)	123.9 (4)	O(1)—C(1)—C(2)	113.1 (4)
O(2)—C(1)—C(2)	122.9 (4)	C(1)—C(2)—C(3)	115.7 (5)

C(2)—C(3)—C(2')	111.9 (5)	O(3)—C(4)—O(4)	124.0 (4)
O(3)—C(4)—C(5)	123.0 (4)	O(4)—C(4)—C(5)	113.0 (4)
C(4)—C(5)—C(6)	116.1 (4)	C(5)—C(6)—C(5')	111.5 (5)
O(5)—C(7)—O(6)	123.2 (4)	O(5)—C(7)—C(8)	121.8 (4)
O(6)—C(7)—C(8)	115.0 (4)	C(7)—C(8)—C(9)	115.3 (4)
C(8)—C(9)—C(8')	111.8 (5)		

Symmetry codes: (i)  $x, -y, z$ ; (ii)  $x, 1 - y, z$ .

The structure of caesium hydrogen carbonate could not be solved by Patterson techniques nor by conventional direct methods, despite exhaustive trials. The structure was elucidated using the symbolic addition procedure *LSAM* (Germain & Woolfson, 1968) programmed into the *MITHRIL* (Gilmore & Brown, 1988) package. Other calculations were made with the *GX* (Mallinson & Muir, 1985) package. The figures were drawn with the aid of the *MOG* (SciTech Software, 1992) program on a Commodore Amiga Computer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and Cs<sup>+</sup>··O distances have been deposited with the IUCr (Reference: MU1051). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## New Crystal Data for [Hg(SC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]

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### Abstract

A new precise determination of the crystal structure of bis(ethanethiolato)mercury reveals a cell [ $a = 7.342(2)$ ,  $b = 4.702(2)$ ,  $c = 23.131(6)$  Å,  $\beta = 101.83(1)^\circ$ ] and

structure slightly different from that reported previously [Bradley & Kunchur (1965). *Can. J. Chem.* **43**, 2786–2792]. The Hg and S atoms lie in planes normal to the crystallographic  $c^*$  axis, separated by the alkyl chains. Weak van der Waals interactions between the alkyl chains give rise to perfect cleavage along the  $ab$  plane. The primary coordination of Hg is linear [Hg—S = 2.343(1) Å, S—Hg—S = 176.48(6)°]. Each Hg atom also takes part in four secondary interactions with S atoms of neighbouring molecules, two at 3.285(1) Å and two at 3.386(1) Å. The total coordination of Hg can be regarded as octahedral with severe tetragonal compression.

### Comment

The majority of bis(thiolato)mercury(II) complexes reported in the literature have essentially linear twofold primary coordination of Hg, with Hg—S bond lengths in the range 2.3–2.4 Å, and weak secondary interactions between monomer units with Hg···S distances in the range 3.0–3.8 Å. These additional long-range interactions are often characteristic of the coordination of Hg with thiolate (and other) ligands.

Of the linearly coordinated compounds reported previously, the structure of [Hg(SC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>], (I), (Bradley & Kunchur, 1965) stood out as being anomalous, with Hg—S bond lengths of 2.45 Å, S—C bond lengths of 1.65 Å and C—C bond lengths of 1.54 and 1.84 Å. The Hg—S bond thus appeared too long, the S—C bond length too short and one C—C distance very long. The cell reported by these authors was monoclinic with  $a = 7.54(2)$ ,  $b = 4.87(1)$ ,  $c = 23.80(4)$  Å,  $\beta = 85^\circ$ , and the space group was reported to be  $Cc$ .

As it is our intention to use the dimensions of these compounds in a study of the coordination geometry exhibited by homoleptic mercury thiolate compounds, we decided to redetermine the structure of this compound in order to obtain more precise data. The structure we report is slightly different to that reported by Bradley & Kunchur (1965).

The crystal structure contains discrete Hg(SC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> molecules in which the primary coordination of Hg is linear [Hg—S = 2.343(1) Å, S—Hg—S = 176.48(6)°], with the Hg atoms lying on the twofold axis. The Hg atoms are approximately hexagonally arranged in a plane normal to  $c^*$  at  $z = \frac{1}{4}$ . On either side is a plane composed of S atoms. Separating these S—Hg—S layers and almost perpendicular to them are the alkyl chains. The S—Hg—S segments are parallel to each other and inclined at 51° to the normal to the Hg plane, with the S atoms 1.47 Å out of this plane. Each Hg atom participates in additional secondary interactions with four S atoms from neighbouring molecules in an approximately square-planar arrangement, two of which are at 3.285(1) Å and two of which are at 3.386(1) Å. The short Hg—S bonds are perpendicular