

Lithium and sodium 3-(3,4-dihydroxyphenyl)propenoate hydrate

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Treatment of 3-(3,4-dihydroxyphenyl)propenoic acid (caffeic acid or 3,4-dihydroxycinnamic acid) with the alkali hydroxides MOH ($M = \text{Li}, \text{Na}$) in aqueous solution led to the formation of poly[aqua[μ -3-(3,4-dihydroxyphenyl)propenoato]lithium], $[\text{Li}(\text{C}_9\text{H}_7\text{O}_4)(\text{H}_2\text{O})]_n$, **1**, and poly[aqua[μ -3-(3,4-dihydroxyphenyl)propenoato]sodium], $[\text{Na}(\text{C}_9\text{H}_7\text{O}_4)(\text{H}_2\text{O})]_n$, **2**. The crystal structure of **1** consists of a lithium cation that is coordinated nearly tetrahedrally by three carboxylate oxygen atoms and a water molecule. The carboxylate groups adopt a μ_3 - $k^3O'O'O'$ coordination mode that leads to a chain-like catenation of Li cations and carboxylate units parallel to the b axis. Moreover, the lithium carboxylate chains are connected by hydrogen bonds between water molecules attached to lithium and catechol OH groups. The crystal structure of **2** shows a sevenfold coordination of the sodium cation by one water molecule, two monodentately binding carboxylate groups and four oxygen atoms from two catechol groups. The coordination polyhedra are linked by face- and edge-sharing into chains extending parallel to the b axis. The chains are interlinked by the bridging 3-(3,4-dihydroxyphenyl)propenoate units and by intermolecular hydrogen bonds to form the tri-periodic network.

1. Chemical context

trans-3-(3,4-Dihydroxyphenyl)-2-propenoic acid (caffeic acid) is ubiquitous in plants and plays a role as an intermediate in the biosynthesis of lignin (Boerjan *et al.*, 2003). The first X-ray crystal-structure analysis of caffeic acid dates back to the year 1987 (García-Granda *et al.*, 1987), and a more recent study was published in 2015 (Kumar *et al.*, 2015). In current research, caffeic acid is used as a co-crystallizing agent, particularly for pharmaceutically relevant compounds such as 5-fluorouracil (Yu *et al.*, 2020). The simultaneous presence of the carboxyl and the catechol moieties renders caffeic acid a versatile ligand in coordination chemistry, in particular after deprotonation of the acidic groups (Petrou *et al.*, 1993). However, transition-metal complexes of caffeic acid derivatives have not yet been structurally investigated. Even for simple alkali metal caffeates, reports are rare and, up to now, only potassium caffeate has been studied in detail as the potassium caffeate/caffeic acid co-crystallization product (Lombardo *et al.*, 2011).

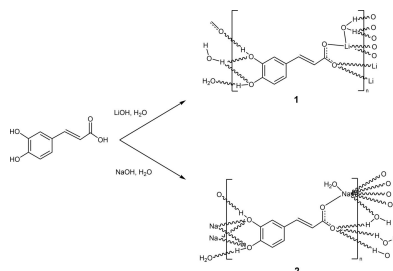
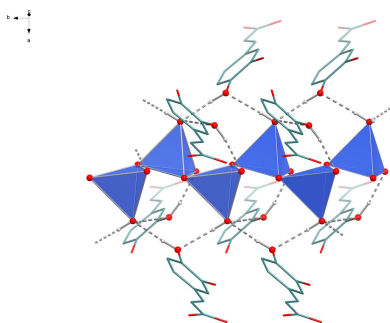


Table 1

Selected geometric parameters (Å, °) for **1**.

C1—C2	1.4855 (18)	C7—O4	1.3781 (16)
C1—O1	1.2669 (16)	Li—O1 ⁱ	1.949 (2)
C1—O2	1.2624 (16)	Li—O1 ⁱⁱⁱ	1.908 (2)
C2—C3	1.3285 (19)	Li—O2	1.962 (2)
C3—C4	1.4685 (18)	Li—O5	2.005 (3)
C6—O3	1.3757 (17)		
O1—C1—C2	117.48 (12)	O1 ⁱ —Li—O5	105.35 (12)
O1 ⁱⁱⁱ —Li—O1 ⁱ	112.20 (11)	O1 ⁱⁱⁱ —Li—O5	109.92 (12)
O1 ⁱ —Li—O2	108.08 (12)	O2—Li—O5	110.08 (11)
O1 ⁱⁱⁱ —Li—O2	111.04 (12)	Li ⁱⁱⁱ —O1—Li ^{iv}	101.15 (8)

Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (ii) $x, y + 1, z$; (iii) $x, y - 1, z$; (iv) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.

Here we report the crystallization and crystal-structure analysis of the lithium and sodium salts of caffeic acid, $\text{LiC}_9\text{H}_7\text{O}_4 \cdot \text{H}_2\text{O}$, **1**, and $\text{NaC}_9\text{H}_7\text{O}_4 \cdot \text{H}_2\text{O}$, **2**, respectively.

2. Structural commentary

The asymmetric unit of **1** comprises one Li cation, one 3-(3,4-dihydroxyphenyl)propenoate anion and one water molecule (Fig. 1). The Li cation is coordinated nearly tetrahedrally by three carboxylate O atoms of three caffeate anions and one water molecule. The Li—O distances range from 1.908 (2) to 2.005 (3) Å and the O—Li—O angles from 105.35 (12) to 112.20 (11)° (Table 1). These values are similar to those reported for other lithium carboxylate compounds such as lithium acetate monohydrate [Li—O: 1.920 (2) to 2.031 (2) Å, O—Li—O: 99.78 (10) to 124.21 (11)°; Martínez Casado *et al.*, 2011]. The carboxylate group adopts a $\mu_3\text{-}\kappa^3\text{O}:\text{O}':\text{O}'$ coordination mode. This leads to the formation of six-membered $\text{Li}_2\text{O}_3\text{C}$ rings that are catenated parallel to the *b* axis by edge-sharing (Fig. 2). Alternatively, the chain structure can be derived from condensation of corner-sharing LiO_4 tetrahedra (Fig. 3). The translational period of the 2_1 -type helix corresponds to the length of the *b* axis and one repeating unit

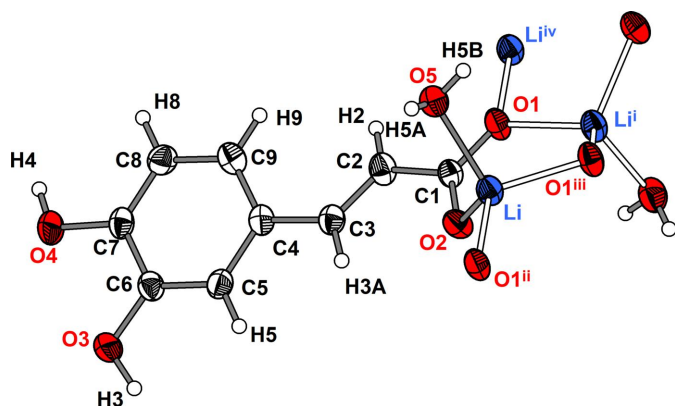


Figure 1

Molecular structure of the (3,4-dihydroxyphenyl)propenoate anion in compound **1** along with the coordination sphere of the lithium cation. The asymmetric unit is displayed with filled bonds. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Symmetry codes refer to Table 1.

Table 2

Continuous shape measurement (CShM) values (*SHAPE 2.1*) for the seven-coordinate sodium ion of **2**.

Heptagon HP-7	32.482
Hexagonal pyramid HPY-7	20.852
Pentagonal bipyramid PBPY-7	5.863
Capped octahedron COC-7	2.807
Capped trigonal prism CTPR-7	3.593
Johnson pentagonal bipyramid JPBPY-7	8.482
Johnson elongated triangular pyramid JETPY-7	20.721

comprises two LiO_4 tetrahedra. Chains of corner-sharing LiO_4 tetrahedra are not unusual for lithium carboxylate monohydrates, and similar patterns were observed for a lithium chloride glycine adduct (Müller *et al.*, 1994) and lithium 2,4,6-trifluorobenzoate hydrate (Lamann *et al.*, 2012), which may serve as representative examples.

In the crystal structure of **2**, the sodium cation adopts a sevenfold coordination from one water oxygen atom, two carboxylate and four catechol oxygen atoms (Fig. 4). According to a SHAPE analysis (*SHAPE 2.1*; Llunell *et al.*, 2013), the NaO_7 polyhedron is roughly related to the face-capped octahedron (CShM 2.807) and to the face-capped trigonal prism (CShM 3.593) with some preference to the former (Llunell *et al.*, 2013; Pinsky & Avnir, 1998; Casanova *et al.*, 2004; Cirera *et al.*, 2005). Numerical data for this analysis

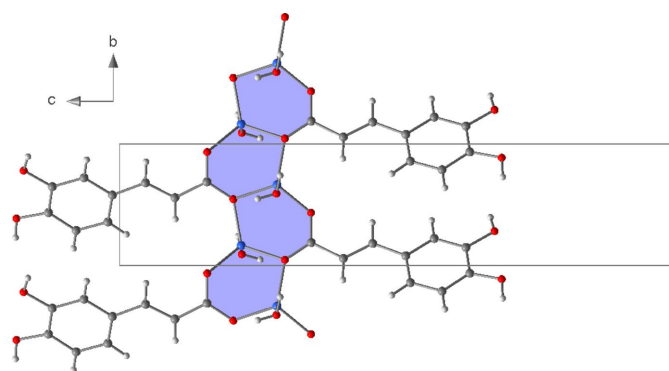


Figure 2

Section of the crystal structure of **1** showing the six-membered $\text{Li}_2\text{O}_3\text{C}$ rings.

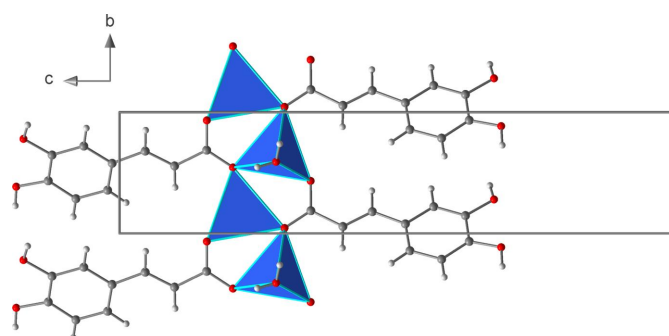


Figure 3

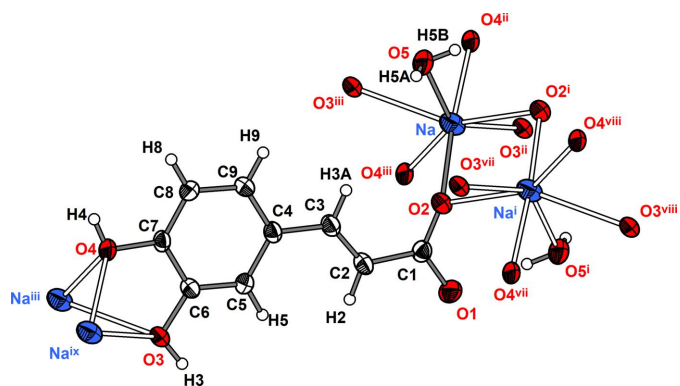
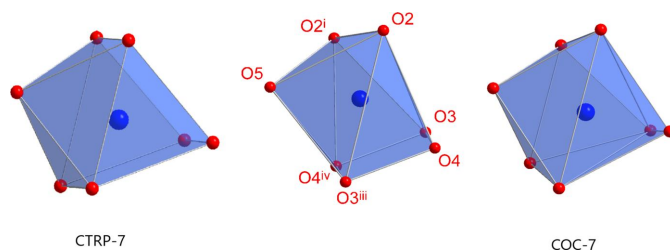
Section of the crystal structure of **1** showing the linkage of the LiO_4 tetrahedra.

Table 3
 Selected geometric parameters (Å, °) for **2**.

C1—C2	1.481 (2)	Na—O2 ⁱ	2.4608 (15)
C1—O2	1.252 (2)	Na—O2	2.3185 (14)
C1—O1	1.282 (2)	Na—O3 ⁱⁱ	2.7897 (17)
C2—C3	1.327 (2)	Na—O3 ⁱⁱⁱ	2.7668 (16)
C3—C4	1.463 (2)	Na—O4 ⁱⁱⁱ	2.5810 (16)
C6—O3	1.3695 (19)	Na—O4 ⁱⁱ	2.4153 (15)
C7—O4	1.3715 (19)	Na—O5	2.4411 (16)
O2—C1—C2	120.37 (14)	O2—Na—O4 ⁱⁱ	175.93 (5)
O2—Na—O2 ⁱ	84.95 (5)	O2—Na—O4 ⁱⁱⁱ	90.18 (5)
O2 ⁱ —Na—O3 ⁱⁱ	83.95 (5)	O2 ⁱ —Na—O4 ⁱⁱⁱ	145.56 (5)
O2—Na—O3 ⁱⁱ	118.94 (5)	O2—Na—O5	92.33 (5)
O2—Na—O3 ⁱⁱⁱ	112.69 (5)	Na—O2—Na ⁱ	95.05 (5)

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

are given in Table 2. The centre of Fig. 5 displays the observed NaO₇ polyhedron and the idealized CTRP-7 (left) and COC-7 (right) polyhedra in order to illustrate the degree of distortion. The Na—O distances are in the range from 2.3185 (14) to 2.7897 (17) Å (Table 3) and are comparable to those found in monosodium tartrate hydrate [2.3331 (12) to 2.6740 (12) Å], which also displays coordination number seven for the sodium cation (Al-Dajani *et al.*, 2010). Generally, sodium carboxylates with coordination number seven for the cation are rather rare. A search of the Cambridge Structural Database (CSD, version 2022.5.43; Groom *et al.*, 2016) gave 20 matches. In this selection, the Na—O distances range from 2.299 to 3.017 Å with a median value of 2.44 Å (lower quartile: 2.380 Å, upper quartile: 2.557 Å). Regarding the coordination mode of the carboxylate unit, the sodium salt **2** differs from the lithium salt **1** in the way that only one carboxylate O atom (O2) is involved in coordination. Furthermore, the coordination mode of the catechol groups is also different in the two structures. In the case of **1**, the catechol groups are part of the hydrogen-bonding network and there is no direct Li—O coordination from these groups. In contrast, the crystal structure of **2** reveals a direct coordination by the catechol oxygen atoms.


Figure 4
 Molecular structure of the caffeate anion in compound **2** along with the coordination sphere of the sodium cation. The asymmetric unit is displayed with filled bonds. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Symmetry codes refer to Table 2. Additional symmetry codes: (vii) $-x + 1, -y, -z + 1$; (viii) $x, y - 1, z + 1$; (ix) $x, y, z - 1$.

Figure 5
 Representation of the NaO₇ polyhedron in **2** (centre) and the best fitting regular polyhedra TRP-7 (left) and COC-7 (right).

Here, the catechol group acts as a chelating ligand and connects two sodium cations. The coordination mode can be described as $\mu\text{-}\kappa^4$ O, O':O, O'. Up to now, sodium compounds with chelating catechol groups have been observed only rarely. The CSD database search resulted in four structures with this coordination motif, *e.g.* in sodium quercetin-5'-sulfonate acetone solvate (Maciołek *et al.*, 2022).

The NaO₇ polyhedra are linked by edge- (O2 and O2ⁱ) and face- (O3ⁱⁱⁱ, O4ⁱⁱⁱ, O3^{iv}, O4^{iv}) sharing to give chains propagating parallel to the *b* axis (Fig. 6). Additional interlinking of these chains by μ_4 -bridging (3,4-dihydroxyphenyl)propenoate units (Fig. 7) leads to layers extending parallel to the *bc* plane.

In the structures of **1** and **2**, the bond lengths and angles within the 3-(3,4-dihydroxyphenyl)propenoate anions are very similar (Tables 1 and 3). The anions are nearly planar apart from a slight tilt [**1**: 6.3 (2)°, **2**: 1.4 (2)°] of the carboxylate group along the C1—C2 bond.

3. Supramolecular features

The supramolecular structure of lithium caffeate hydrate is governed by O—H...O hydrogen bonds (Table 4). Both hydrogen atoms H5A and H5B of the water molecule are involved in hydrogen bonds to adjacent catechol groups

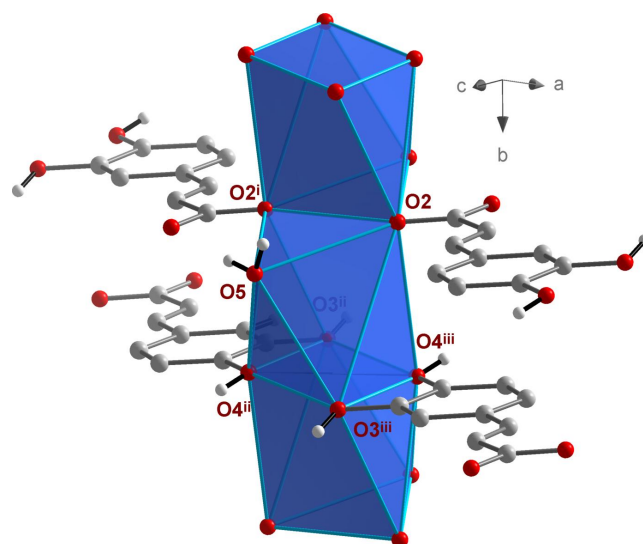

Figure 6
 Linkage of the NaO₇ polyhedra by edge- and face-sharing in the crystal structure of **2**.

Table 4
Hydrogen-bond geometry (Å, °) for **1**.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O3—H3···O2 ^v	0.92 (2)	1.83 (2)	2.734 (2)	168 (2)
O4—H4···O5 ^{vi}	0.88 (2)	1.94 (2)	2.793 (2)	160.7 (2)
O5—H5A···O4 ^{vii}	0.85 (3)	2.13 (2)	2.977 (2)	173 (2)
O5—H5B···O3 ^{viii}	0.80 (2)	2.33 (2)	3.042 (2)	150 (2)
O5—H5B···O4 ^{viii}	0.80 (2)	2.33 (2)	2.953 (2)	136 (2)

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

(Fig. 8). H5B is part of a bifurcated hydrogen bond that connects the catechol oxygen atoms O3 and O4 with the water oxygen atom O5 (type a_1 and a_2 in Fig. 8). H5A forms a hydrogen bond to another neighbouring catechol oxygen atom O4 (type b). Moreover, the water oxygen atom O5 acts as an acceptor for the O4—H4 hydroxyl group of a further catechol unit in the surrounding (type c). An additional type of hydrogen bond is formed between the catechol group O3—H3 as the donor and the carboxylate oxygen atom O2 as an acceptor (type d). The corresponding hydrogen bonds can be

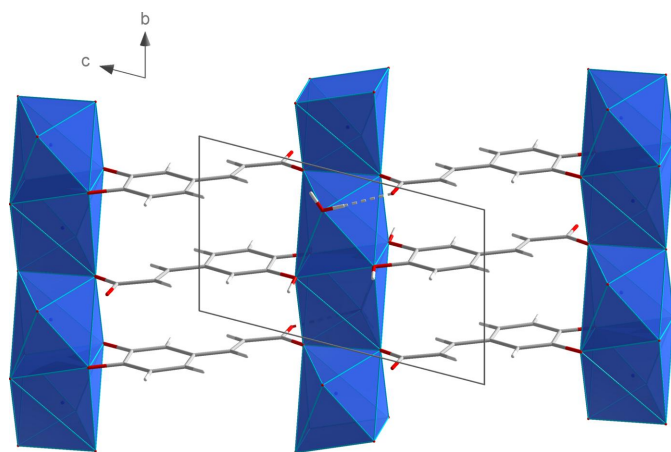


Figure 7
Linkage of the NaO₇ polyhedral chains by (3,4-dihydroxyphenyl) propenoate units in the crystal structure of **2**.

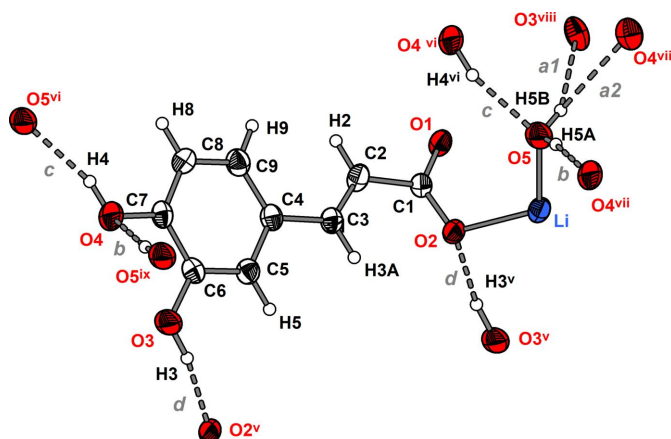


Figure 8
Hydrogen-bonding patterns in **1**. Symmetry codes refer to Table 4. Additional symmetry codes: (x) $-x + 2, -y, -z$; (xi) $x + 1, y, z$; (xii) $x - 2, -y, -z + 1$.

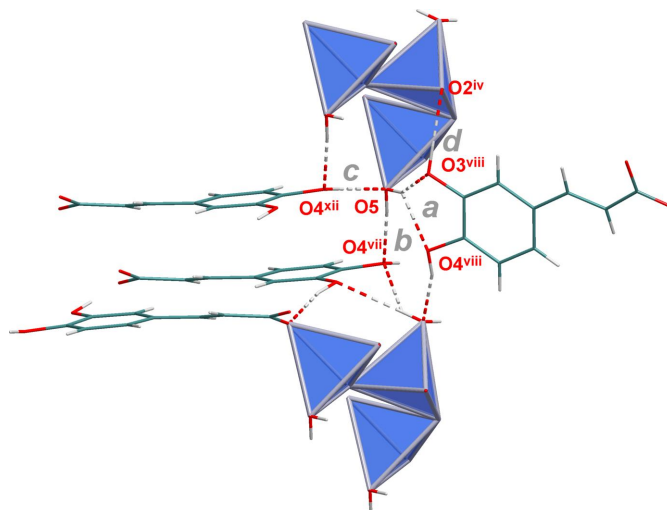


Figure 9
Interconnection of the LiO₄ tetrahedra chains of **1** by hydrogen bonds (dashed lines). Symmetry codes refer to Tables 1 and 4. Additional symmetry code: (xii) $x - 2, -y, -z + 1$.

considered as medium-strong to weak, with the shortest O···O distance found for the d type [2.734 (2) Å] hydrogen bond and the largest for the bifurcated a_1 type hydrogen bond [3.042 (2) Å].

Regarding the LiO₄ tetrahedra chains, the hydrogen bonds are essential for intra-chain and inter-chain supramolecular organization. Within a chain, directly adjacent LiO₄ tetrahedra are linked pairwise (1,2 connection) by a sequence of hydrogen bonds of the type a_1 – d starting from O5 (Figs. 9, 10). Additionally, there is a c – b hydrogen-bonding sequence starting from O5 that links two LiO₄ tetrahedra, which are separated by one LiO₄ unit (1,3 connection). The interconnection of the LiO₄ tetrahedra chains is based on two a_2 – c

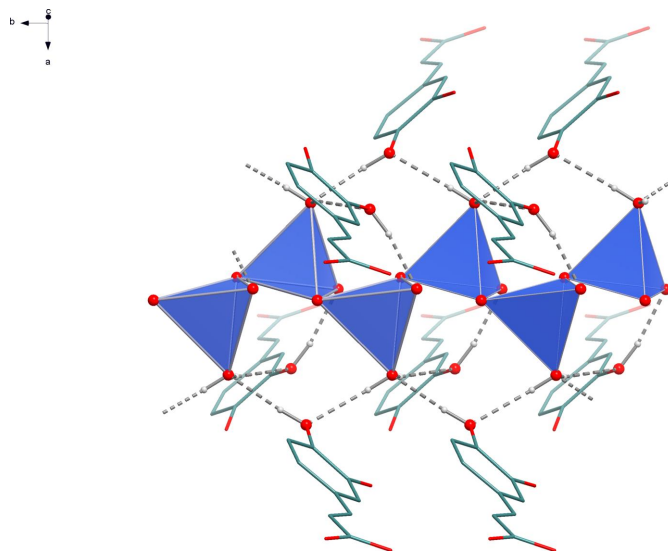


Figure 10
Position of the hydrogen bonds (dashed lines) along the LiO₄ tetrahedra chains in the crystal structure of **1**.

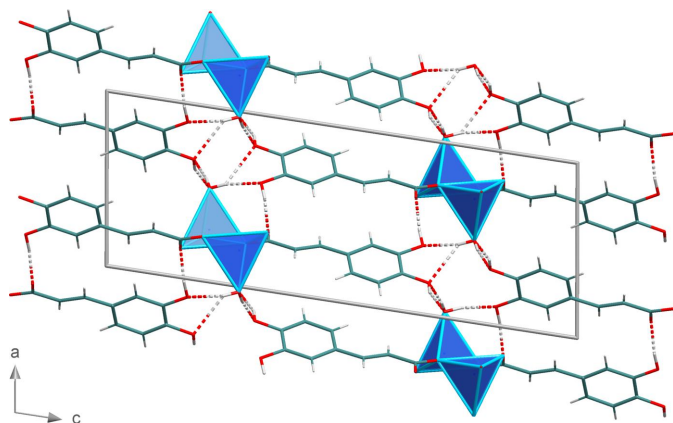


Figure 11
Section of the crystal structure of **1** with the complete hydrogen-bonding network.

hydrogen-bonding sequences starting from O5 or its centrosymmetric equivalent in the neighbouring chain. This leads to $R_2^2(24)$ motifs (Fig. 11).

As in the case of **1**, O—H...O hydrogen bonds are essential for the supramolecular organisation within the crystal structure of **2** (Table 5). The water molecule (H5A—O1—H5B) participates in two hydrogen bonds (Fig. 12). The hydrogen bond O5^{xi}—H5B^{xi}...O1 with the carboxylate oxygen atom as an acceptor (equivalent to O5^{xi}—H5B^{xi}...O1^{xii}, type *a* in Fig. 12) acts as an intra-layer linkage, and the hydrogen bond O5^{xi}—H5A^{xi}—O1 (equivalent to O5ⁱ—H5Aⁱ...O1^{xii}, type *b* in Fig. 12) connects adjacent layers (Fig. 13).

Fig. 14 represents the position of the intra-chain hydrogen bonds. Furthermore, the catechol groups are involved in hydrogen-bonding interactions. The O3—H3 group acts as the

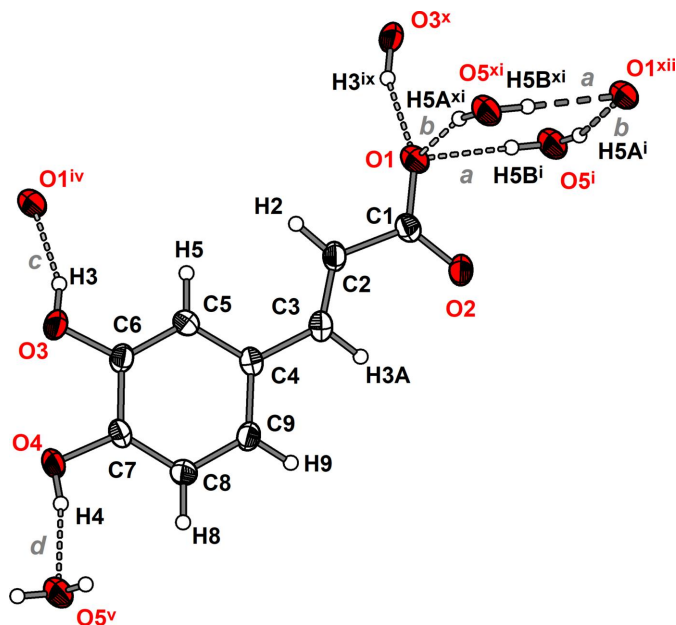


Figure 12
Hydrogen-bonding patterns in the crystal structure of **2**. Symmetry codes refer to Table 5.

Table 5
Hydrogen-bond geometry (Å, °) for **2**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3...O1 ^{iv}	0.84 (2)	1.84 (2)	2.6437 (19)	158 (2)
O4—H4...O5 ^v	0.81 (2)	1.85 (2)	2.6350 (19)	166 (2)
O5—H5A...O1 ^{vi}	0.83 (2)	2.02 (2)	2.826 (2)	163 (2)
O5—H5B...O1 ⁱ	0.82 (2)	1.95 (2)	2.7614 (19)	178 (3)

Symmetry codes: (i) $-x + 1, -y, -z + 1$; (iv) $-x + 2, -y, -z$; (v) $-x, -y + 1, -z$; (vi) $x - 1, y, z$.

donor with respect to the carboxylate oxygen atom O1 of a neighbouring chain (O^{iv} in Fig. 12, type *c*). This leads to an $R_2^2(18)$ motif between adjacent 3-(3,4-dihydroxyphenyl)-2-propenoate units (Fig. 13). Finally, the cross-linking of the

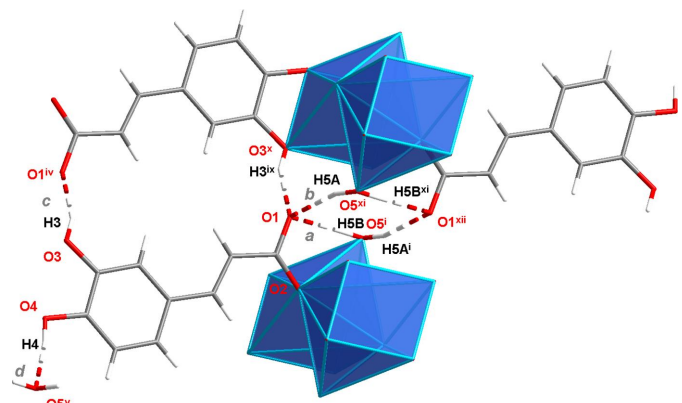


Figure 13
Inter-layer hydrogen bonds in **2**. Symmetry codes refer to Table 5.

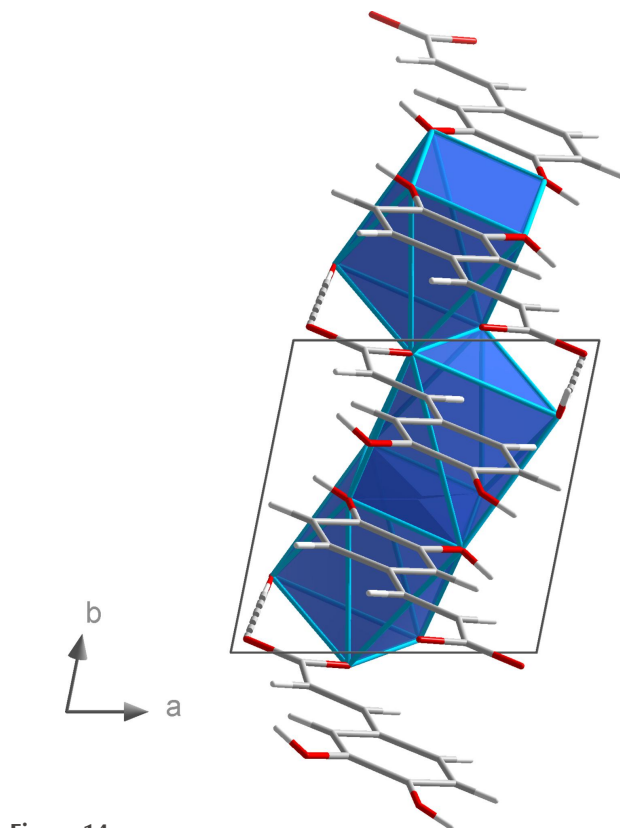


Figure 14
Intra-chain hydrogen bonds in compound **2**.

Table 6
Experimental details.

	1	2
Crystal data		
Chemical formula	[Li(C ₉ H ₇ O ₄)(H ₂ O)]	[Na(C ₉ H ₇ O ₄)(H ₂ O)]
<i>M_r</i>	204.10	220.15
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Triclinic, <i>P</i> 1̄
Temperature (K)	220	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.3083 (12), 4.8511 (5), 22.587 (4)	6.3289 (13), 6.8126 (14), 11.253 (2)
<i>α</i> , <i>β</i> , <i>γ</i> (°)	90, 98.572 (18), 90	75.05 (2), 86.39 (2), 78.09 (2)
<i>V</i> (Å ³)	900.2 (2)	458.64 (17)
<i>Z</i>	4	2
Radiation type	Mo <i>Kα</i>	Mo <i>Kα</i>
<i>μ</i> (mm ⁻¹)	0.12	0.17
Crystal size (mm)	0.46 × 0.15 × 0.15	0.4 × 0.2 × 0.08
Data collection		
Diffractometer	Stoe <i>IPDS</i> 2	Stoe <i>IPDS</i> 2
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	4973, 1735, 1314	7192, 1798, 1331
<i>R</i> _{int}	0.027	0.048
(sin θ/λ) _{max} (Å ⁻¹)	0.619	0.619
Refinement		
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.032, 0.079, 1.01	0.035, 0.095, 1.00
No. of reflections	1735	1798
No. of parameters	152	152
No. of restraints	0	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.19, -0.15	0.24, -0.22

Computer programs: *X-AREA* (Stoe & Cie, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *DIAMOND* (Brandenburg & Putz, 2019) and *OLEX2* (Dolomanov *et al.*, 2009).

chains is completed by hydrogen bonds of the type *d* with the O4–H4 group as the donor and the water oxygen atom O5 of a neighbouring chain as acceptor. The position of the different hydrogen-bonding types is displayed in Fig. 15. Fig. 16 shows a packing diagram with the complete hydrogen-bonding network of **2**. In direct comparison with **1**, the hydrogen bonds in **2** are significantly stronger, with the closest O...O distance being 2.6350 (19) Å (Table 5).

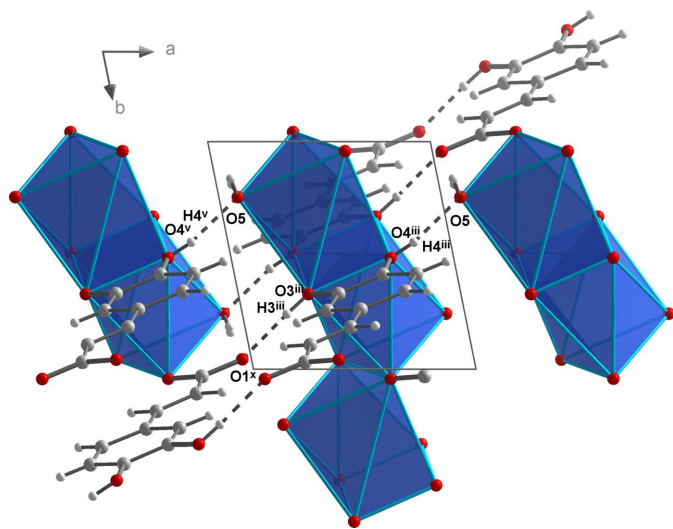


Figure 15
Position of the hydrogen bonds (dashed lines) along the NaO₇ polyhedral chains in the crystal structure of **2**. Symmetry codes refer to Table 3. Additional symmetry codes: (x) *x* - 1, *y* + 1, *z*; (xi) *x* + 1, *y*, *z*.

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 2022.3; Groom *et al.*, 2016) for metal caffeates revealed only the crystal structure of the potassium caffeate/caffeic acid co-crystallization product (CSD code GIFXEA; Lombardo *et al.*, 2012). Furthermore, there are 16 crystal structures containing caffeic acid as free acid, hydrate or co-crystals with various organic molecules.

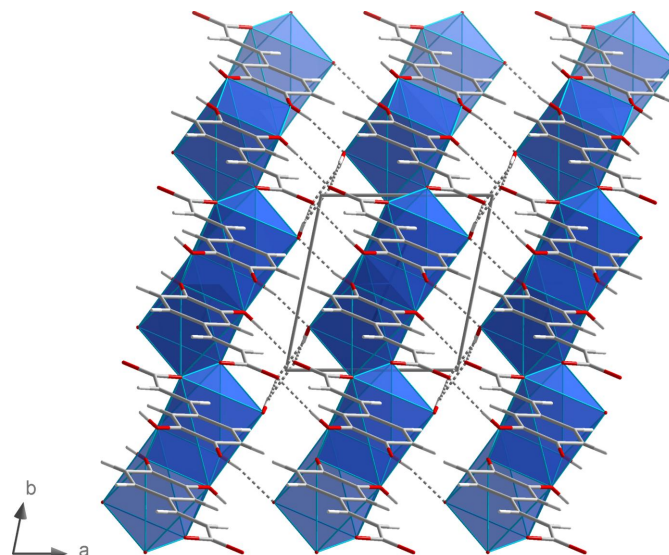


Figure 16
Section of the crystal structure of **2** showing the complete hydrogen-bonding network (dashed lines).

5. Synthesis and crystallization

2 mmol of the alkali hydroxide (48 mg, LiOH, 80 mg NaOH) and 2 mmol of caffeic acid (360 mg) were dissolved in 5 ml of water to give a clear solution. After slow evaporation the products were isolated as colourless solids in nearly quantitative yield. Single crystals were obtained by recrystallization from water.

Compound **1**: IR: 1643 *m*, 1616 *w*, 1548 *s*, 1524 *m*, 1441 *w*, 1401 *vs*, 1360 *w*, 1304 *w*, 1249 *vs*, 1195 *w*, 1164 *s*, 1109 *s*, 971 *s*, 859 *s*, 809 *s*, 714 *s*, 602 *w*, 581 *s* cm⁻¹.

Compound **2**: IR: 1641 *m*, 1601 *m*, 1519 *s*, 1474 *w*, 1409 *w*, 1369 *s*, 1290 *w*, 1273 *m*, 1250 *s*, 1224 *w*, 1195 *m*, 1012 *w*, 969 *s*, 829 *w*, 873 *w*, 859 *m*, 814 *s*, 739 *m*, 695 *m*, 600 *m*, 564 *s*, 516 *m* cm⁻¹.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 6. All carbon-bound hydrogen atoms were positioned geometrically (C–H = 0.94 Å) and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Hydrogen atoms bound to oxygen were found in difference-Fourier maps. The O–H distances of **2** were restricted to 0.82 Å.

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Lithium and sodium 3-(3,4-dihydroxyphenyl)propenoate hydrate

Irén Bieler, Christoph Wagner and Kurt Merzweiler

Computing details

Poly[aqua[μ -3-(3,4-dihydroxyphenyl)propenoato]lithium] (1)*Crystal data*

[Li(C₉H₇O₄)(H₂O)]
 $M_r = 204.10$
 Monoclinic, $P2_1/n$
 $a = 8.3083$ (12) Å
 $b = 4.8511$ (5) Å
 $c = 22.587$ (4) Å
 $\beta = 98.572$ (18)°
 $V = 900.2$ (2) Å³
 $Z = 4$

$F(000) = 424$
 $D_x = 1.506$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 3964 reflections
 $\theta = 2.5$ – 26.0 °
 $\mu = 0.12$ mm⁻¹
 $T = 220$ K
 Block, colourless
 $0.46 \times 0.15 \times 0.15$ mm

Data collection

Stoe IPDS 2
 diffractometer
 Radiation source: sealed X-ray tube, 12 x 0.4
 mm long-fine focus, Incoatec I μ s
 Plane graphite monochromator
 Detector resolution: 6.67 pixels mm⁻¹
 rotation method scans
 4973 measured reflections

1735 independent reflections
 1314 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.027$
 $\theta_{max} = 26.1$ °, $\theta_{min} = 2.5$ °
 $h = -10 \rightarrow 10$
 $k = -5 \rightarrow 5$
 $l = -27 \rightarrow 27$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.079$
 $S = 1.01$
 1735 reflections
 152 parameters
 0 restraints

Primary atom site location: structure-invariant
 direct methods
 Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 0.0259P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.19$ e Å⁻³
 $\Delta\rho_{min} = -0.15$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.71575 (16)	0.1874 (3)	0.65653 (5)	0.0232 (3)
C2	0.74035 (18)	0.0573 (3)	0.59901 (6)	0.0297 (3)
H2	0.787147	-0.119367	0.599929	0.036*
C3	0.69907 (16)	0.1798 (3)	0.54634 (6)	0.0274 (3)
H3A	0.647720	0.352195	0.547117	0.033*
C4	0.72381 (16)	0.0791 (3)	0.48705 (6)	0.0265 (3)
C5	0.64958 (16)	0.2210 (3)	0.43618 (6)	0.0279 (3)
H5	0.579486	0.369071	0.440744	0.034*
C6	0.67740 (16)	0.1475 (3)	0.37929 (6)	0.0272 (3)
C7	0.78474 (16)	-0.0658 (3)	0.37246 (6)	0.0271 (3)
C8	0.85657 (17)	-0.2130 (3)	0.42205 (6)	0.0307 (3)
H8	0.926536	-0.360889	0.417203	0.037*
C9	0.82555 (18)	-0.1427 (3)	0.47885 (6)	0.0315 (3)
H9	0.873489	-0.245454	0.512161	0.038*
Li	0.7956 (3)	0.6632 (5)	0.71799 (10)	0.0283 (5)
O1	0.75014 (12)	0.0450 (2)	0.70375 (4)	0.0297 (3)
O2	0.66671 (12)	0.43357 (19)	0.65694 (4)	0.0294 (3)
O3	0.60783 (14)	0.2806 (2)	0.32801 (4)	0.0376 (3)
H3	0.525 (3)	0.395 (4)	0.3355 (9)	0.060 (6)*
O4	0.81610 (14)	-0.1140 (3)	0.31514 (4)	0.0362 (3)
H4	0.869 (3)	-0.271 (5)	0.3134 (9)	0.068 (7)*
O5	1.03368 (14)	0.5915 (3)	0.71894 (5)	0.0361 (3)
H5A	1.082 (3)	0.740 (6)	0.7122 (11)	0.092 (9)*
H5B	1.070 (3)	0.548 (5)	0.7522 (11)	0.070 (7)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0269 (7)	0.0219 (7)	0.0211 (7)	-0.0027 (6)	0.0043 (5)	0.0003 (5)
C2	0.0412 (8)	0.0232 (7)	0.0258 (7)	-0.0006 (6)	0.0089 (6)	-0.0027 (6)
C3	0.0281 (7)	0.0301 (8)	0.0245 (7)	-0.0019 (6)	0.0056 (5)	-0.0028 (6)
C4	0.0272 (7)	0.0298 (8)	0.0232 (7)	-0.0049 (6)	0.0056 (5)	-0.0021 (6)
C5	0.0265 (7)	0.0327 (8)	0.0255 (7)	0.0004 (6)	0.0068 (5)	-0.0031 (6)
C6	0.0268 (7)	0.0327 (8)	0.0217 (7)	-0.0033 (6)	0.0026 (5)	-0.0009 (5)
C7	0.0276 (7)	0.0323 (8)	0.0222 (7)	-0.0048 (6)	0.0063 (5)	-0.0052 (6)
C8	0.0329 (8)	0.0283 (8)	0.0314 (7)	0.0030 (7)	0.0061 (6)	-0.0039 (6)
C9	0.0377 (8)	0.0315 (8)	0.0249 (7)	-0.0022 (7)	0.0034 (6)	0.0005 (6)
Li	0.0389 (13)	0.0229 (11)	0.0239 (11)	0.0025 (10)	0.0075 (9)	-0.0009 (9)
O1	0.0468 (6)	0.0226 (5)	0.0208 (5)	0.0037 (4)	0.0087 (4)	0.0015 (4)
O2	0.0406 (6)	0.0227 (5)	0.0242 (5)	0.0047 (5)	0.0019 (4)	-0.0011 (4)
O3	0.0420 (6)	0.0486 (7)	0.0220 (5)	0.0132 (6)	0.0038 (4)	0.0016 (5)
O4	0.0455 (6)	0.0419 (7)	0.0229 (5)	0.0066 (6)	0.0106 (4)	-0.0046 (5)
O5	0.0378 (6)	0.0444 (7)	0.0261 (6)	0.0060 (6)	0.0049 (5)	0.0005 (5)

Geometric parameters (Å, °)

C1—C2	1.4855 (18)	C7—O4	1.3781 (16)
C1—O1	1.2669 (16)	C8—H8	0.9400
C1—O2	1.2624 (16)	C8—C9	1.388 (2)
C2—H2	0.9400	C9—H9	0.9400
C2—C3	1.3285 (19)	Li—Li ⁱ	2.979 (3)
C3—H3A	0.9400	Li—Li ⁱ	2.979 (3)
C3—C4	1.4685 (18)	Li—O1 ⁱⁱ	1.949 (2)
C4—C5	1.401 (2)	Li—O1 ⁱⁱⁱ	1.908 (2)
C4—C9	1.398 (2)	Li—O2	1.962 (2)
C5—H5	0.9400	Li—O5	2.005 (3)
C5—C6	1.3857 (18)	O3—H3	0.92 (2)
C6—C7	1.390 (2)	O4—H4	0.88 (3)
C6—O3	1.3757 (17)	O5—H5A	0.85 (3)
C7—C8	1.386 (2)	O5—H5B	0.79 (3)
O1—C1—C2	117.48 (12)	C8—C9—H9	119.6
O2—C1—C2	119.66 (12)	Li ⁱ —Li—Li ⁱⁱ	109.00 (13)
O2—C1—O1	122.83 (12)	O1 ⁱⁱⁱ —Li—Li ⁱⁱ	39.93 (3)
C1—C2—H2	118.6	O1 ⁱⁱⁱ —Li—Li ⁱ	144.46 (14)
C3—C2—C1	122.84 (13)	O1 ⁱⁱ —Li—Li ⁱ	38.92 (9)
C3—C2—H2	118.6	O1 ⁱⁱ —Li—Li ⁱⁱ	72.61 (11)
C2—C3—H3A	116.0	O1 ⁱⁱⁱ —Li—O1 ⁱⁱ	112.20 (11)
C2—C3—C4	127.96 (14)	O1 ⁱⁱ —Li—O2	108.08 (12)
C4—C3—H3A	116.0	O1 ⁱⁱⁱ —Li—O2	111.04 (12)
C5—C4—C3	118.68 (13)	O1 ⁱⁱ —Li—O5	105.35 (12)
C9—C4—C3	123.15 (12)	O1 ⁱⁱⁱ —Li—O5	109.92 (12)
C9—C4—C5	118.07 (12)	O2—Li—Li ⁱ	74.16 (8)
C4—C5—H5	119.3	O2—Li—Li ⁱⁱ	130.66 (15)
C6—C5—C4	121.35 (14)	O2—Li—O5	110.08 (11)
C6—C5—H5	119.3	O5—Li—Li ⁱ	100.11 (11)
C5—C6—C7	119.53 (12)	O5—Li—Li ⁱⁱ	117.27 (13)
O3—C6—C5	123.57 (13)	C1—O1—Li ^{iv}	133.25 (11)
O3—C6—C7	116.87 (11)	C1—O1—Li ⁱ	123.58 (11)
C8—C7—C6	120.01 (12)	Li ^{iv} —O1—Li ⁱ	101.15 (8)
O4—C7—C6	116.41 (12)	C1—O2—Li	113.53 (11)
O4—C7—C8	123.56 (13)	C6—O3—H3	111.2 (12)
C7—C8—H8	119.9	C7—O4—H4	110.7 (14)
C7—C8—C9	120.23 (13)	Li—O5—H5A	110.0 (18)
C9—C8—H8	119.9	Li—O5—H5B	106.7 (16)
C4—C9—H9	119.6	H5A—O5—H5B	106 (2)
C8—C9—C4	120.72 (13)		
C1—C2—C3—C4	176.94 (13)	C5—C6—C7—O4	-175.22 (12)
C2—C1—O1—Li ^{iv}	-12.6 (2)	C6—C7—C8—C9	-2.0 (2)
C2—C1—O1—Li ⁱ	-173.12 (12)	C7—C8—C9—C4	-1.0 (2)
C2—C1—O2—Li	-131.35 (13)	C9—C4—C5—C6	-0.9 (2)

C2—C3—C4—C5	170.59 (14)	O1—C1—C2—C3	175.69 (13)
C2—C3—C4—C9	-13.2 (2)	O1—C1—O2—Li	46.58 (17)
C3—C4—C5—C6	175.49 (13)	O2—C1—C2—C3	-6.3 (2)
C3—C4—C9—C8	-173.87 (13)	O2—C1—O1—Li ^{iv}	169.48 (14)
C4—C5—C6—C7	-1.9 (2)	O2—C1—O1—Li ⁱ	8.9 (2)
C4—C5—C6—O3	-179.85 (13)	O3—C6—C7—C8	-178.57 (13)
C5—C4—C9—C8	2.4 (2)	O3—C6—C7—O4	2.84 (18)
C5—C6—C7—C8	3.4 (2)	O4—C7—C8—C9	176.53 (13)

Symmetry codes: (i) $-x+3/2, y-1/2, -z+3/2$; (ii) $-x+3/2, y+1/2, -z+3/2$; (iii) $x, y+1, z$; (iv) $x, y-1, z$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3 \cdots O2 ^v	0.92 (2)	1.83 (2)	2.734 (2)	168 (2)
O4—H4 \cdots O5 ^{vi}	0.88 (2)	1.94 (2)	2.793 (2)	160.7 (2)
O5—H5A \cdots O4 ^{vii}	0.85 (3)	2.13 (2)	2.977 (2)	173 (2)
O5—H5B \cdots O3 ^{viii}	0.80 (2)	2.33 (2)	3.042 (2)	150 (2)
O5—H5B \cdots O4 ^{viii}	0.80 (2)	2.33 (2)	2.953 (2)	136 (2)

Symmetry codes: (v) $-x+1, -y+1, -z+1$; (vi) $-x+2, -y, -z+1$; (vii) $-x+2, -y+1, -z+1$; (viii) $x+1/2, -y+1/2, z+1/2$.

Poly[aqua[μ -3-(3,4-dihydroxyphenyl)propenoato]sodium] (2)

Crystal data

[Na(C₉H₇O₄)(H₂O)]
 $M_r = 220.15$
 Triclinic, $P\bar{1}$
 $a = 6.3289$ (13) \AA
 $b = 6.8126$ (14) \AA
 $c = 11.253$ (2) \AA
 $\alpha = 75.05$ (2) $^\circ$
 $\beta = 86.39$ (2) $^\circ$
 $\gamma = 78.09$ (2) $^\circ$
 $V = 458.64$ (17) \AA^3

$Z = 2$
 $F(000) = 228$
 $D_x = 1.594$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA
 Cell parameters from 2529 reflections
 $\theta = 3.1\text{--}26.0^\circ$
 $\mu = 0.17$ mm⁻¹
 $T = 293$ K
 Plate, colourless
 $0.4 \times 0.2 \times 0.08$ mm

Data collection

Stoe IPDS 2
 diffractometer
 Radiation source: sealed X-ray tube, 12 x 0.4
 mm long-fine focus, Incoatec $I\mu$ s
 Plane graphite monochromator
 Detector resolution: 6.67 pixels mm⁻¹
 rotation method scans
 7192 measured reflections

1798 independent reflections
 1331 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.048$
 $\theta_{\text{max}} = 26.1^\circ$, $\theta_{\text{min}} = 3.2^\circ$
 $h = -7 \rightarrow 7$
 $k = -8 \rightarrow 8$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.095$
 $S = 1.00$
 1798 reflections
 152 parameters

4 restraints
 Primary atom site location: dual
 Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0615P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.7621 (3)	0.0311 (2)	0.28917 (15)	0.0254 (4)
C2	0.7226 (3)	0.1072 (2)	0.15528 (14)	0.0264 (4)
H2	0.8399	0.1004	0.1013	0.032*
C3	0.5262 (3)	0.1847 (2)	0.10941 (15)	0.0255 (4)
H3A	0.4138	0.1903	0.1666	0.031*
C4	0.4642 (3)	0.2624 (2)	-0.01989 (14)	0.0227 (3)
C5	0.6151 (3)	0.2576 (2)	-0.11683 (15)	0.0251 (4)
H5	0.7604	0.2042	-0.0994	0.030*
C6	0.5499 (3)	0.3310 (2)	-0.23713 (14)	0.0251 (4)
C7	0.3322 (3)	0.4163 (2)	-0.26497 (14)	0.0228 (3)
C8	0.1815 (3)	0.4196 (2)	-0.17098 (14)	0.0259 (4)
H8	0.0363	0.4734	-0.1888	0.031*
C9	0.2482 (3)	0.3420 (2)	-0.04956 (14)	0.0260 (4)
H9	0.1458	0.3434	0.0134	0.031*
Na	0.44737 (11)	0.27100 (10)	0.47948 (6)	0.0348 (2)
O1	0.95808 (19)	-0.0433 (2)	0.32325 (11)	0.0363 (3)
O2	0.60826 (19)	0.04183 (18)	0.36431 (10)	0.0328 (3)
O3	0.6857 (2)	0.3298 (2)	-0.33673 (11)	0.0387 (3)
H3	0.800 (3)	0.243 (4)	-0.314 (2)	0.070 (8)*
O4	0.2845 (2)	0.48950 (18)	-0.38767 (10)	0.0304 (3)
H4	0.164 (3)	0.558 (3)	-0.391 (2)	0.053 (7)*
O5	0.0849 (2)	0.2438 (2)	0.43233 (13)	0.0345 (3)
H5A	0.070 (4)	0.163 (3)	0.391 (2)	0.061 (8)*
H5B	0.070 (4)	0.187 (4)	0.5048 (17)	0.059 (7)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0297 (9)	0.0243 (8)	0.0217 (8)	-0.0013 (6)	-0.0040 (6)	-0.0074 (6)
C2	0.0302 (9)	0.0310 (8)	0.0179 (8)	-0.0074 (7)	0.0019 (6)	-0.0054 (6)
C3	0.0320 (9)	0.0251 (8)	0.0190 (8)	-0.0054 (6)	0.0016 (6)	-0.0054 (6)
C4	0.0291 (8)	0.0213 (7)	0.0177 (8)	-0.0046 (6)	-0.0009 (6)	-0.0048 (6)
C5	0.0235 (8)	0.0271 (8)	0.0220 (8)	-0.0018 (6)	-0.0030 (6)	-0.0031 (6)
C6	0.0274 (8)	0.0261 (8)	0.0197 (8)	-0.0039 (6)	0.0036 (6)	-0.0042 (6)
C7	0.0293 (9)	0.0215 (7)	0.0164 (8)	-0.0023 (6)	-0.0033 (6)	-0.0042 (6)
C8	0.0238 (8)	0.0268 (8)	0.0240 (9)	0.0009 (6)	-0.0024 (6)	-0.0050 (6)
C9	0.0278 (8)	0.0287 (8)	0.0199 (8)	-0.0025 (6)	0.0035 (6)	-0.0066 (6)

Na	0.0381 (4)	0.0366 (4)	0.0316 (4)	-0.0084 (3)	0.0087 (3)	-0.0132 (3)
O1	0.0302 (7)	0.0487 (7)	0.0270 (7)	0.0046 (5)	-0.0078 (5)	-0.0123 (5)
O2	0.0343 (7)	0.0399 (7)	0.0195 (6)	0.0017 (5)	0.0019 (5)	-0.0068 (5)
O3	0.0304 (7)	0.0546 (8)	0.0191 (6)	0.0056 (6)	0.0051 (5)	-0.0004 (5)
O4	0.0323 (7)	0.0360 (6)	0.0165 (6)	0.0050 (5)	-0.0046 (5)	-0.0033 (5)
O5	0.0356 (7)	0.0375 (7)	0.0262 (7)	-0.0005 (5)	-0.0078 (5)	-0.0039 (6)

Geometric parameters (Å, °)

C1—C2	1.481 (2)	Na—Na ⁱⁱ	3.4689 (15)
C1—O2	1.252 (2)	Na—O2 ⁱ	2.4608 (15)
C1—O1	1.282 (2)	Na—O2	2.3185 (14)
C2—H2	0.9300	Na—O3 ⁱⁱⁱ	2.7897 (17)
C2—C3	1.327 (2)	Na—O3 ^{iv}	2.7668 (16)
C3—H3A	0.9300	Na—O4 ^{iv}	2.5810 (16)
C3—C4	1.463 (2)	Na—O4 ⁱⁱⁱ	2.4153 (15)
C4—C5	1.406 (2)	Na—O5	2.4411 (16)
C4—C9	1.390 (2)	Na—H5B	2.55 (2)
C5—H5	0.9300	O2—Na ⁱ	2.4608 (15)
C5—C6	1.374 (2)	O3—Na ^v	2.7897 (17)
C6—C7	1.401 (2)	O3—Na ^{iv}	2.7669 (16)
C6—O3	1.3695 (19)	O3—H3	0.841 (17)
C7—C8	1.380 (2)	O4—Na ^{iv}	2.5810 (16)
C7—O4	1.3715 (19)	O4—Na ^v	2.4153 (15)
C8—H8	0.9300	O4—H4	0.803 (16)
C8—C9	1.390 (2)	O5—H5A	0.827 (17)
C9—H9	0.9300	O5—H5B	0.816 (17)
Na—Na ⁱ	3.5262 (15)		
O1—C1—C2	117.18 (14)	O3 ⁱⁱⁱ —Na—Na ⁱⁱ	51.08 (4)
O2—C1—C2	120.37 (14)	O3 ^{iv} —Na—Na ⁱ	151.40 (5)
O2—C1—O1	122.45 (15)	O3 ⁱⁱⁱ —Na—Na ⁱ	104.16 (5)
C1—C2—H2	118.8	O3 ^{iv} —Na—Na ⁱⁱ	51.67 (4)
C3—C2—C1	122.43 (15)	O3 ^{iv} —Na—O3 ⁱⁱⁱ	102.74 (4)
C3—C2—H2	118.8	O3 ^{iv} —Na—H5B	94.7 (5)
C2—C3—H3A	116.0	O3 ⁱⁱⁱ —Na—H5B	126.0 (4)
C2—C3—C4	128.09 (15)	O4 ⁱⁱⁱ —Na—Na ⁱ	132.15 (5)
C4—C3—H3A	116.0	O4 ⁱⁱⁱ —Na—Na ⁱⁱ	48.03 (4)
C5—C4—C3	122.50 (15)	O4 ^{iv} —Na—Na ⁱⁱ	44.09 (3)
C9—C4—C3	119.45 (14)	O4 ^{iv} —Na—Na ⁱ	125.28 (5)
C9—C4—C5	118.04 (14)	O4 ⁱⁱⁱ —Na—O2 ⁱ	91.26 (5)
C4—C5—H5	119.7	O4 ^{iv} —Na—O3 ^{iv}	57.67 (4)
C6—C5—C4	120.66 (15)	O4 ⁱⁱⁱ —Na—O3 ^{iv}	71.38 (4)
C6—C5—H5	119.7	O4 ^{iv} —Na—O3 ⁱⁱⁱ	68.74 (4)
C5—C6—C7	120.37 (15)	O4 ⁱⁱⁱ —Na—O3 ⁱⁱⁱ	59.01 (4)
O3—C6—C5	124.36 (15)	O4 ⁱⁱⁱ —Na—O4 ^{iv}	92.12 (5)
O3—C6—C7	115.27 (14)	O4 ⁱⁱⁱ —Na—O5	88.31 (5)
C8—C7—C6	119.71 (14)	O4 ^{iv} —Na—H5B	152.3 (5)

O4—C7—C6	115.86 (14)	O4 ⁱⁱⁱ —Na—H5B	80.0 (5)
O4—C7—C8	124.43 (14)	O5—Na—Na ⁱ	83.14 (5)
C7—C8—H8	120.2	O5—Na—Na ⁱⁱ	121.25 (5)
C7—C8—C9	119.57 (14)	O5—Na—O2 ⁱ	77.91 (5)
C9—C8—H8	120.2	O5—Na—O3 ^{iv}	81.58 (5)
C4—C9—H9	119.2	O5—Na—O3 ⁱⁱⁱ	142.21 (5)
C8—C9—C4	121.62 (15)	O5—Na—O4 ^{iv}	136.45 (5)
C8—C9—H9	119.2	O5—Na—H5B	18.6 (4)
Na ⁱⁱ —Na—Na ⁱ	153.76 (5)	C1—O2—Na	136.46 (11)
Na ⁱⁱ —Na—H5B	122.5 (6)	C1—O2—Na ⁱ	119.95 (10)
Na ⁱ —Na—H5B	77.2 (5)	Na—O2—Na ⁱ	95.05 (5)
O2—Na—Na ⁱ	44.04 (4)	C6—O3—Na ^v	106.29 (10)
O2 ⁱ —Na—Na ⁱ	40.91 (3)	C6—O3—Na ^{iv}	101.08 (9)
O2—Na—Na ⁱⁱ	134.17 (5)	C6—O3—H3	108.4 (19)
O2 ⁱ —Na—Na ⁱⁱ	128.97 (5)	Na ^{iv} —O3—Na ^v	77.26 (4)
O2—Na—O2 ⁱ	84.95 (5)	Na ^{iv} —O3—H3	140.1 (19)
O2 ⁱ —Na—O3 ⁱⁱⁱ	83.95 (5)	Na ^v —O3—H3	117.7 (19)
O2—Na—O3 ⁱⁱⁱ	118.94 (5)	C7—O4—Na ^v	116.66 (9)
O2—Na—O3 ^{iv}	112.69 (5)	C7—O4—Na ^{iv}	105.73 (10)
O2 ⁱ —Na—O3 ^{iv}	153.47 (5)	C7—O4—H4	105.9 (17)
O2—Na—O4 ⁱⁱⁱ	175.93 (5)	Na ^v —O4—Na ^{iv}	87.88 (5)
O2—Na—O4 ^{iv}	90.18 (5)	Na ^v —O4—H4	127.7 (17)
O2 ⁱ —Na—O4 ^{iv}	145.56 (5)	Na ^{iv} —O4—H4	109.1 (17)
O2—Na—O5	92.33 (5)	Na—O5—H5A	119.7 (18)
O2—Na—H5B	99.4 (5)	Na—O5—H5B	88.4 (18)
O2 ⁱ —Na—H5B	61.8 (5)	H5A—O5—H5B	108 (2)
C1—C2—C3—C4	-179.15 (14)	C6—C7—O4—Na ^{iv}	-50.68 (14)
C2—C1—O2—Na	-94.99 (19)	C6—C7—O4—Na ^v	44.96 (17)
C2—C1—O2—Na ⁱ	126.10 (13)	C7—C6—O3—Na ^{iv}	46.19 (15)
C2—C3—C4—C5	2.1 (3)	C7—C6—O3—Na ^v	-33.62 (16)
C2—C3—C4—C9	-178.71 (16)	C7—C8—C9—C4	0.6 (2)
C3—C4—C5—C6	179.58 (14)	C8—C7—O4—Na ^v	-134.11 (14)
C3—C4—C9—C8	179.34 (14)	C8—C7—O4—Na ^{iv}	130.25 (14)
C4—C5—C6—C7	1.5 (2)	C9—C4—C5—C6	0.4 (2)
C4—C5—C6—O3	-179.20 (15)	O1—C1—C2—C3	179.07 (15)
C5—C4—C9—C8	-1.5 (2)	O1—C1—O2—Na ⁱ	-54.4 (2)
C5—C6—C7—C8	-2.3 (2)	O1—C1—O2—Na	84.5 (2)
C5—C6—C7—O4	178.54 (14)	O2—C1—C2—C3	-1.4 (2)
C5—C6—O3—Na ^{iv}	-133.17 (15)	O3—C6—C7—C8	178.27 (15)
C5—C6—O3—Na ^v	147.02 (14)	O3—C6—C7—O4	-0.8 (2)
C6—C7—C8—C9	1.3 (2)	O4—C7—C8—C9	-179.66 (14)

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3 \cdots O1 ^{vi}	0.84 (2)	1.84 (2)	2.6437 (19)	158 (2)

O4—H4···O5 ^{vii}	0.81 (2)	1.85 (2)	2.6350 (19)	166 (2)
O5—H5A···O1 ^{viii}	0.83 (2)	2.02 (2)	2.826 (2)	163 (2)
O5—H5B···O1 ⁱ	0.82 (2)	1.95 (2)	2.7614 (19)	178 (3)

Symmetry codes: (i) $-x+1, -y, -z+1$; (vi) $-x+2, -y, -z$; (vii) $-x, -y+1, -z$; (viii) $x-1, y, z$.