



Lithium dipotassium citrate monohydrate, $\text{LiK}_2\text{C}_6\text{H}_5\text{O}_7(\text{H}_2\text{O})$

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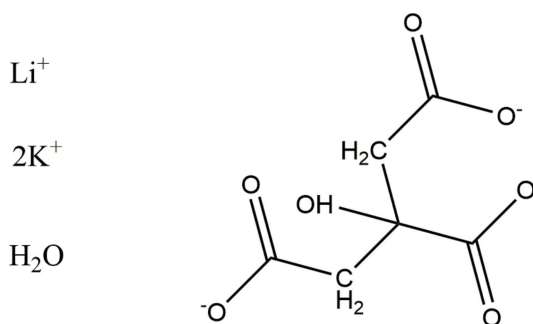
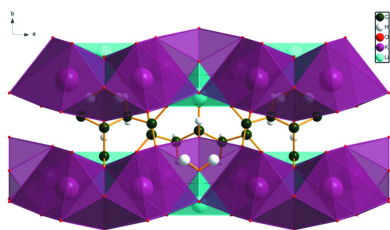
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The crystal structure of dilithium potassium citrate monohydrate, $\text{Li}^+\cdot 2\text{K}^+\cdot \text{C}_6\text{H}_5\text{O}_7^{3-}\cdot \text{H}_2\text{O}$ or $\text{LiK}_2\text{C}_6\text{H}_5\text{O}_7\cdot \text{H}_2\text{O}$, has been solved by direct methods and refined against laboratory X-ray powder diffraction data, and optimized using density functional techniques. The complete citrate trianion is generated by a crystallographic mirror plane, with two C and three O atoms lying on the reflecting plane, and chelates to three different K cations. The KO_8 and LiO_4 coordination polyhedra share edges and corners to form layers lying parallel to the *ac* plane. An intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond occurs between the hydroxyl group and the central carboxylate group of the citrate anion as well as a charge-assisted intermolecular $\text{O}-\text{H}\cdots\text{O}$ link between the water molecule and the terminal carboxylate group. There is also a weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond.

1. Chemical context

A systematic study of the crystal structures of Group 1 (alkali metal) citrate salts has been reported in Rammohan & Kaduk (2018). The study was extended to lithium hydrogen citrates in Cigler & Kaduk (2018), to sodium hydrogen citrates in Cigler & Kaduk (2019*a*), to sodium dirubidium citrates in Cigler & Kaduk (2019*b*) and to dilithium potassium citrate (Cigler & Kaduk, 2019*c*). We now report the synthesis and structure of the title compound, $\text{LiK}_2\text{C}_6\text{H}_5\text{O}_7(\text{H}_2\text{O})$, which represents a further extension to lithium dipotassium citrates.



2. Structural commentary

The structure of $\text{LiK}_2\text{C}_6\text{H}_5\text{O}_7(\text{H}_2\text{O})$ was solved and refined from powder data and optimized by density functional theory (DFT) calculations (see *Experimental* section) and is illustrated in Fig. 1. The root-mean-square Cartesian displacement of the non-hydrogen atoms in the refined and optimized

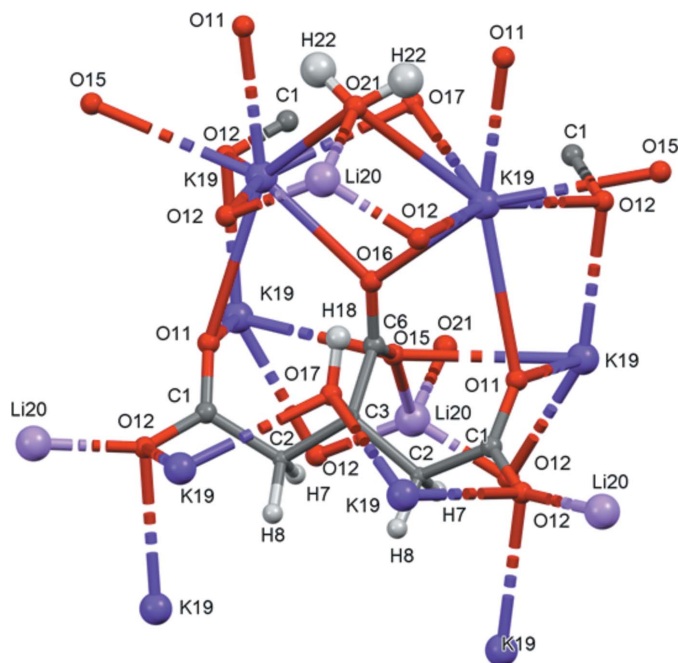


Figure 1
The crystal structure of $\text{LiK}_2\text{C}_6\text{H}_5\text{O}_7(\text{H}_2\text{O})$ with the atom numbering and 50% probability spheroids.

structures is 0.047 \AA (Fig. 2). The excellent agreement between the structures is evidence that the experimental structure is correct (van de Streek & Neumann, 2014). All of the citrate bond distances, bond angles, and torsion angles fall within the normal ranges indicated by a *Mercury* Mogul geometry check (Macrae *et al.*, 2020). The citrate anion occurs in the *trans,trans*-conformation (about C2–C3 and the symmetry-related atoms), which is one of the two low-energy conformations of an isolated citrate anion (Rammohan & Kaduk, 2018). Since C3, the central C6/O15/O16 carboxylate

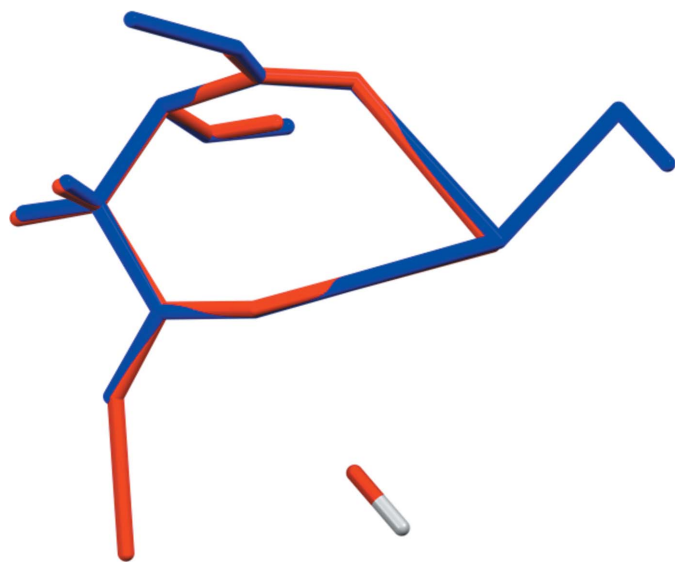


Figure 2
Comparison of the refined and optimized structures of $\text{LiK}_2\text{C}_6\text{H}_5\text{O}_7(\text{H}_2\text{O})$. The refined structure is in red, and the DFT-optimized structure is in blue.

Table 1
Hydrogen-bond geometry (\AA , $^\circ$) for kadu1697_DFT.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O21-H22}\cdots\text{O11}$	0.98	1.73	2.687	164
$\text{O17-H18}\cdots\text{O16}$	0.98	1.90	2.581	124
$\text{C2-H7}\cdots\text{O11}^i$	1.09	2.47	3.396	142

Symmetry code: (i) $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$.

group and the O17–H18 hydroxy group lie on the mirror plane, they exhibit the normal planar arrangement. The Mulliken overlap populations indicate that both the Li–O and K–O bonds have some covalent character, but that the Li–O bonds are more covalent.

The $\text{C}_6\text{H}_5\text{O}_7^{3-}$ citrate anion doubly chelates to three different K19 ions through O11/O16, O11/O15 and O12/O17. Each citrate oxygen atom bridges multiple metal atoms. K19 is eight-coordinate (irregular), with a bond-valence sum (in valence units) of 1.04 and Li20 (site symmetry m) is tetrahedral with a bond-valence sum of 1.10. Atom O21 of the water molecule of crystallization also lies on a (100) mirror plane.

The Bravais–Friedel–Donnay–Harker (Bravais, 1866; Friedel, 1907; Donnay & Harker, 1937) method suggests that we might expect a blocky morphology for lithium dipotassium citrate monohydrate. A 2nd order spherical harmonic preferred orientation model was included in the refinement; the texture index was 1.000, indicating that preferred orientation was not present for this rotated capillary specimen.

3. Supramolecular features

The KO_8 and LiO_4 coordination polyhedra share edges and corners to form layers lying parallel to the ac plane (Fig. 3). The only traditional hydrogen bonds are an intramolecular O17–H18 \cdots O16 interaction between the hydroxyl group and the central carboxylate group (Table 1), and a charge-assisted hydrogen bond between the water molecule O21–H22 and O11. By the correlation of Rammohan & Kaduk (2018), these hydrogen bonds contribute 13.2 and $13.4 \text{ kcal mol}^{-1}$, respec-

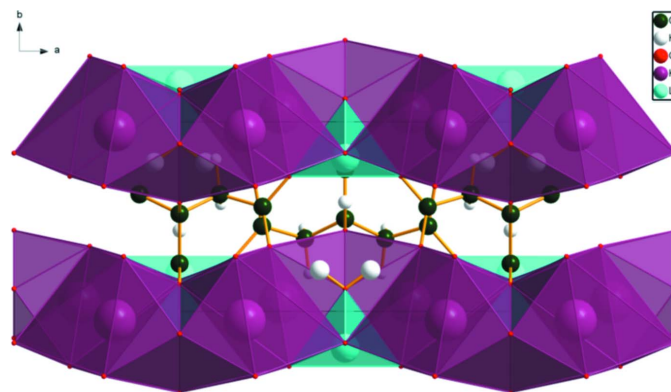


Figure 3
The crystal structure of $\text{LiK}_2\text{C}_6\text{H}_5\text{O}_7(\text{H}_2\text{O})$, viewed down the c axis.

tively, to the crystal energy. There is also a weak C2—H7···O11 hydrogen bond (Table 1).

4. Database survey

Details of the comprehensive literature search for citrate structures are presented in Rammohan & Kaduk (2018). A reduced cell search in the Cambridge Structural Database (Groom *et al.*, 2016) yielded two hits, but no citrate structures. A few weak unindexed peaks were identified as 2.0 wt% dilithium potassium citrate (Cigler & Kaduk, 2019c).

5. Synthesis and crystallization

Masses of 0.3777 g of Li₂CO₃ (5.00 mmol, Sigma-Aldrich) and 1.3851 g of K₂CO₃ (10.0 mmol, Sigma-Aldrich) were added to a solution of 2.0325 g of citric acid (10.0 mmol, Sigma-Aldrich) monohydrate in 15 ml of water. After the fizzing subsided, the clear solution was dried first at 450 K to yield a sticky solid. The solid was heated at 477 K to yield a white foam. Further heating at 505 K yielded additional expansion of the foam, and slight discoloration. This foam was amorphous. Storage of the foam under ambient conditions yielded a puddle. Heating this puddle to 394 K yielded a glassy solid. Adding two drops of water to this solid yielded a paste, which yielded the title compound as a crystalline white powder after heating to 394 K for 15 min.

6. Refinement

The pattern of LiK₂C₆H₅O₇(H₂O) was indexed using *Jade* 9.8 (MDI, 2017). *EXPO2014* (Altomare *et al.*, 2013) suggested the

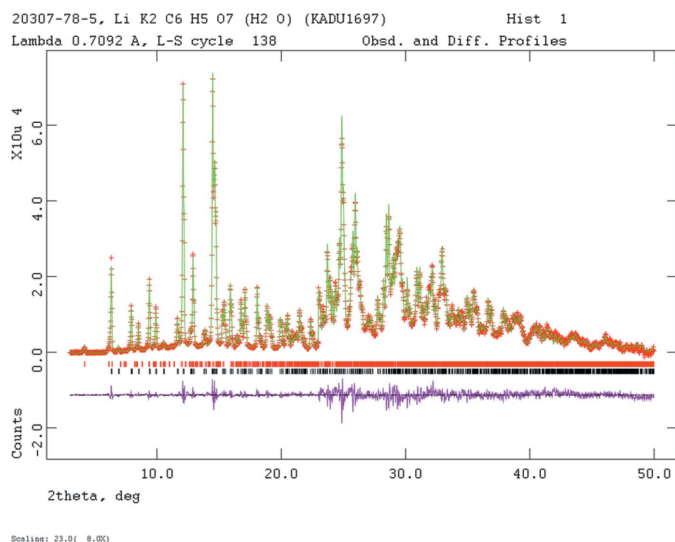


Figure 4 Observed, calculated, and difference patterns of LiK₂C₆H₅O₇(H₂O). The red crosses represent the observed data points, the green solid line the calculated pattern, and the magenta line the difference (observed - calculated) pattern. The vertical scale is multiplied by a factor of 8 above 23° 2θ.

Table 2 Experimental details.

KADU1697_phase_1	
Crystal data	
Chemical formula	Li ⁺ ·2K ⁺ ·C ₆ H ₅ O ₇ ³⁻ ·H ₂ O
<i>M_r</i>	292.25
Crystal system, space group	Orthorhombic, <i>Pmn</i> 2 ₁
Temperature (K)	300
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.24878 (19), 5.86577 (14), 8.19290 (16)
<i>V</i> (Å ³)	492.53 (1)
<i>Z</i>	2
Radiation type	<i>K</i> α ₁ , <i>K</i> α ₂ , λ = 0.709237, 0.713647 Å
Specimen shape, size (mm)	Cylinder, 12 × 0.7
Data collection	
Diffractometer	PANalytical Empyrean
Specimen mounting	Glass capillary
Data collection mode	Transmission
Scan method	Step
2θ values (°)	2θ _{min} = 1.008, 2θ _{max} = 49.988, 2θ _{step} = 0.017
Refinement	
<i>R</i> factors and goodness of fit	<i>R_p</i> = 0.034, <i>R_{wp}</i> = 0.044, <i>R_{exp}</i> = 0.015, <i>R</i> (<i>F</i> ²) = 0.04860, χ ² = 8.940
No. of parameters	56
No. of restraints	14
(Δ/σ) _{max}	0.49

Computer programs: *EXPO2014* (Altomare *et al.*, 2013), *GSAS* (Toby & Von Dreele, 2013), *Mercury* (Macrae *et al.*, 2020), *DIAMOND* (Crystal Impact, 2015), and *publCIF* (Westrip, 2010).

space group *Pmn*2₁, which was confirmed by successful solution and refinement of the structure. The structure of LiK₂C₆H₅O₇(H₂O) was solved by direct methods as implemented in *EXPO2014* (Altomare *et al.*, 2013), which located all the non-hydrogen atoms including the lithium atom. The positions of H7 and H8 were calculated using *Materials Studio* (Dassault, 2018). The position of the active hydrogen atom H18 was deduced from the potential intramolecular hydrogen-bonding pattern, and the position of H22 was deduced from the hydrogen-bonding pattern. Pseudo-Voigt profile coefficients were as parameterized in Thompson *et al.* (1987) and the asymmetry correction of Finger *et al.* (1994) was applied and the microstrain broadening model of Stephens (1999). The hydrogen atoms were included in fixed positions, which were re-calculated during the course of the refinement using *Materials Studio*. Crystal data, data collection and structure refinement (Fig. 4) details are summarized in Table 2. The *U*_{iso} values for C2 and C3 were constrained to be equal, and those of H7 and H8 were constrained to be 1.3× that of these carbon atoms. The *U*_{iso} of C1, C5, C6 and the oxygen atoms were constrained to be equal, and that of H18 was constrained to be 1.3× this value. The background was modeled by a three-term shifted Chebyshev polynomial. A ten-term diffuse scattering function was used to describe the scattering from the capillary and any amorphous material. The structure of dilithium potassium citrate, Li₂KC₆H₅O₇ (Cigler & Kaduk, 2019c), was included as a second phase in the Rietveld refinement but its atomic positional and displacement parameters were not refined.

A density functional geometry optimization was carried out using *CRYSTAL14* (Dovesi *et al.*, 2014). The basis sets for the H, C, N, and O atoms were those of Gatti *et al.* (1994), and the basis set for K was that of Peintinger *et al.* (2013). The calculation was run on eight 2.1 GHz Xeon cores (each with 6 Gb RAM) of a 304-core Dell Linux cluster at IIT, using 8 *k*-points and the B3LYP functional, and took two hours.

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Lithium dipotassium citrate monohydrate, $\text{LiK}_2\text{C}_6\text{H}_5\text{O}_7(\text{H}_2\text{O})$

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Computing details

Program(s) used to solve structure: *EXPO2014* (Altomare *et al.*, 2013) for KADU1697_phase_1; known structure for KADU1697_phase_2. Molecular graphics: *Mercury* (Macrae *et al.*, 2020), *DIAMOND* (Crystal Impact, 2015) for KADU1697_phase_1. Software used to prepare material for publication: *publCIF* (Westrip, 2010) for KADU1697_phase_1.

Lithium dipotassium citrate monohydrate (KADU1697_phase_1)

Crystal data

$\text{Li}^+ \cdot 2\text{K}^+ \cdot \text{C}_6\text{H}_5\text{O}_7^{3-} \cdot \text{H}_2\text{O}$

$M_r = 292.25$

Orthorhombic, *Pmn*2₁

Hall symbol: P 2ac -2

$a = 10.24878$ (19) Å

$b = 5.86577$ (14) Å

$c = 8.19290$ (16) Å

$V = 492.53$ (1) Å³

$Z = 2$

$D_x = 1.971$ Mg m⁻³

$T = 300$ K

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.2488 (7)	0.5454 (12)	0.9115 (17)	0.0155 (10)*
C2	0.1204 (5)	0.6153 (14)	0.8359 (11)	0.010 (2)*
C3	0.0	0.5097 (15)	0.9185	0.010 (2)*
C6	0.0	0.2480 (14)	0.8941 (14)	0.0155 (10)*
H7	0.125	0.5784	0.7037	0.013 (3)*
H8	0.1091	0.8242	0.8467	0.013 (3)*
O11	0.2709 (4)	0.3382 (8)	0.9343 (12)	0.0155 (10)*
O12	0.3320 (4)	0.6995 (7)	0.9364 (12)	0.0155 (10)*
O15	0.0	0.1757 (12)	0.7512 (12)	0.0155 (10)*
O16	0.0	0.1310 (11)	1.0247 (12)	0.0155 (10)*
O17	0.0	0.5645 (12)	1.0886 (8)	0.0155 (10)*
H18	0.0	0.4231	1.1176	0.0201 (13)*
K19	0.20108 (18)	-0.0384 (3)	1.1763 (10)	0.0333 (7)*
Li20	0.0	0.213 (4)	1.526 (3)	0.04*
O21	0.5	0.1259 (10)	0.9430 (16)	0.018 (3)*
H22	0.4268	0.1937	0.9402	0.04*

Geometric parameters (Å, °)

C1—C2	1.510 (3)	O16—C6	1.271 (6)
C1—O11	1.250 (5)	O16—K19	2.604 (4)
C1—O12	1.260 (6)	O16—K19 ⁱ	2.604 (4)
C2—C1	1.510 (3)	O17—C3	1.430 (7)
C2—C3	1.538 (3)	O17—H18	0.863 (7)
C2—H7	1.105 (10)	O17—K19 ⁱⁱⁱ	3.192 (5)
C2—H8	1.234 (8)	O17—K19 ^{viii}	3.192 (5)
C3—C2	1.538 (3)	H18—O17	0.863 (7)
C3—C2 ⁱ	1.538 (3)	K19—H8 ^{ix}	2.704 (4)
C3—C6	1.548 (3)	K19—O11	3.053 (5)
C3—O17	1.430 (7)	K19—O11 ^x	2.765 (5)
C6—C3	1.548 (3)	K19—O12 ^{xi}	2.833 (5)
C6—O15	1.245 (7)	K19—O12 ^{ix}	2.934 (5)
C6—O16	1.271 (6)	K19—O15 ^{xii}	3.226 (3)
H7—C2	1.105 (10)	K19—O16	2.604 (4)
H8—C2	1.234 (8)	K19—O17 ^{xi}	3.192 (5)
O11—C1	1.250 (5)	K19—O21 ^{xiii}	3.047 (7)
O11—K19	3.053 (5)	Li20—O12 ^{xiv}	1.941 (12)
O11—K19 ⁱⁱ	2.765 (5)	Li20—O12 ^{ix}	1.941 (12)
O12—C1	1.260 (6)	Li20—O15 ^{xv}	1.86 (2)
O12—K19 ⁱⁱⁱ	2.833 (5)	Li20—O21 ^{xiii}	2.11 (2)
O12—K19 ^{iv}	2.934 (5)	O21—K19 ^{xvi}	3.047 (7)
O12—Li20 ^v	1.941 (12)	O21—K19 ⁱⁱ	3.047 (7)
O15—C6	1.245 (7)	O21—Li20 ^{xvi}	2.11 (2)
O15—K19 ^{vi}	3.226 (3)	O21—H22 ^{xvii}	0.908 (5)
O15—K19 ⁱⁱ	3.226 (3)	O21—H22 ^{ix}	0.908 (5)
O15—Li20 ^{vii}	1.86 (2)	H22—O21 ^{xviii}	0.908 (5)
C2—C1—O11	118.9 (6)	O11—K19—O12 ^{xi}	80.28 (12)
C2—C1—O12	117.5 (6)	O11—K19—O12 ^{ix}	90.49 (12)
O11—C1—O12	123.4 (6)	O11—K19—O15 ^{xii}	94.67 (13)
C1—C2—C3	114.1 (5)	O11—K19—O16	66.39 (15)
C1—C2—H7	108.2 (6)	O11—K19—O17 ^{xi}	122.22 (14)
C1—C2—H8	108.8 (6)	O11—K19—O21 ^{xiii}	138.24 (16)
C3—C2—H7	112.7 (6)	O11 ^x —K19—O12 ^{xi}	97.83 (17)
C3—C2—H8	107.0 (6)	O11 ^x —K19—O12 ^{ix}	83.53 (13)
H7—C2—H8	105.6 (5)	O11 ^x —K19—O15 ^{xii}	66.25 (14)
C2—C3—C2 ⁱ	106.8 (6)	O11 ^x —K19—O16	133.62 (19)
C2—C3—C6	110.0 (5)	O11 ^x —K19—O17 ^{xi}	77.00 (13)
C2—C3—O17	109.8 (5)	O11 ^x —K19—O21 ^{xiii}	54.18 (14)
C2 ⁱ —C3—C6	110.0 (5)	O12 ^{xi} —K19—O12 ^{ix}	157.86 (7)
C2 ⁱ —C3—O17	109.8 (5)	O12 ^{xi} —K19—O15 ^{xii}	63.05 (15)
C6—C3—O17	110.4 (7)	O12 ^{xi} —K19—O16	104.54 (18)
C3—C6—O15	117.3 (8)	O12 ^{xi} —K19—O17 ^{xi}	75.75 (14)
C3—C6—O16	115.3 (8)	O12 ^{xi} —K19—O21 ^{xiii}	136.58 (15)
O15—C6—O16	127.4 (9)	O12 ^{ix} —K19—O15 ^{xii}	98.08 (14)

C1—O11—K19	139.3 (6)	O12 ^{ix} —K19—O16	89.80 (17)
C1—O11—K19 ⁱⁱ	121.5 (6)	O12 ^{ix} —K19—O17 ^{xi}	125.68 (15)
K19—O11—K19 ⁱⁱ	93.48 (13)	O12 ^{ix} —K19—O21 ^{xiii}	61.00 (17)
C1—O12—K19 ⁱⁱⁱ	100.4 (5)	O15 ^{xii} —K19—O16	159.7 (2)
C1—O12—K19 ^{iv}	106.9 (5)	O15 ^{xii} —K19—O17 ^{xi}	118.28 (14)
C1—O12—Li20 ^v	148.3 (8)	O15 ^{xii} —K19—O21 ^{xiii}	117.64 (16)
K19 ⁱⁱⁱ —O12—K19 ^{iv}	94.68 (12)	O16—K19—O17 ^{xi}	70.13 (18)
K19 ⁱⁱⁱ —O12—Li20 ^v	90.8 (7)	O16—K19—O21 ^{xiii}	82.6 (2)
K19 ^{iv} —O12—Li20 ^v	101.5 (7)	O17 ^{xi} —K19—O21 ^{xiii}	66.53 (17)
C6—O15—K19 ^{vi}	105.29 (16)	O12 ^{xiv} —Li20—O12 ^{ix}	125.0 (14)
C6—O15—K19 ⁱⁱ	105.29 (16)	O12 ^{xiv} —Li20—O15 ^{xv}	114.1 (8)
C6—O15—Li20 ^{vii}	153.2 (10)	O12 ^{xiv} —Li20—O21 ^{xiii}	97.2 (8)
K19 ^{vi} —O15—K19 ⁱⁱ	143.4 (2)	O12 ^{ix} —Li20—O15 ^{xv}	114.1 (8)
K19 ^{vi} —O15—Li20 ^{vii}	80.9 (3)	O12 ^{ix} —Li20—O21 ^{xiii}	97.2 (8)
K19 ⁱⁱ —O15—Li20 ^{vii}	80.9 (3)	O15 ^{xv} —Li20—O21 ^{xiii}	102.1 (11)
C6—O16—K19	127.43 (14)	K19 ^{xvi} —O21—K19 ⁱⁱ	85.1 (2)
C6—O16—K19 ⁱ	127.43 (14)	K19 ^{xvi} —O21—Li20 ^{xvi}	94.2 (5)
K19—O16—K19 ⁱ	104.7 (3)	K19 ^{xvi} —O21—H22 ^{xvii}	64.4 (7)
C3—O17—H18	93.0 (6)	K19 ^{xvi} —O21—H22 ^{ix}	132.6 (7)
C3—O17—K19 ⁱⁱⁱ	112.5 (4)	K19 ⁱⁱ —O21—Li20 ^{xvi}	94.2 (5)
C3—O17—K19 ^{viii}	112.5 (4)	K19 ⁱⁱ —O21—H22 ^{xvii}	132.6 (7)
H18—O17—K19 ⁱⁱⁱ	129.8 (3)	K19 ⁱⁱ —O21—H22 ^{ix}	64.4 (7)
H18—O17—K19 ^{viii}	129.8 (3)	Li20 ^{xvi} —O21—H22 ^{xvii}	55.8 (4)
K19 ⁱⁱⁱ —O17—K19 ^{viii}	80.43 (16)	Li20 ^{xvi} —O21—H22 ^{ix}	55.8 (4)
O11—K19—O11 ^x	158.80 (9)	H22 ^{xvii} —O21—H22 ^{ix}	110.0 (8)

Symmetry codes: (i) $-x, y, z$; (ii) $-x+1/2, -y, z-1/2$; (iii) $x, y+1, z$; (iv) $-x+1/2, -y+1, z-1/2$; (v) $x+1/2, -y+1, z-1/2$; (vi) $x-1/2, -y, z-1/2$; (vii) $x, y, z-1$; (viii) $-x, y+1, z$; (ix) $-x+1/2, -y+1, z+1/2$; (x) $-x+1/2, -y, z+1/2$; (xi) $x, y-1, z$; (xii) $x+1/2, -y, z+1/2$; (xiii) $x-1/2, -y, z+1/2$; (xiv) $x-1/2, -y+1, z+1/2$; (xv) $x, y, z+1$; (xvi) $x+1/2, -y, z-1/2$; (xvii) $x+1/2, -y+1, z+1/2$; (xviii) $x-1/2, -y+1, z-1/2$.

(KADU1697_phase_2)

Crystal data

$C_6H_5KLi_2O_7$

$M_r = 242.08$

Triclinic, $P\bar{1}$

$a = 6.48415 \text{ \AA}$

$b = 6.68334 \text{ \AA}$

$c = 9.81709 \text{ \AA}$

$\alpha = 87.6373^\circ$

$\beta = 80.6064^\circ$

$\gamma = 83.1095^\circ$

$V = 416.59 \text{ \AA}^3$

$Z = 2$

$D_x = 1.930 \text{ Mg m}^{-3}$

$T = 300 \text{ K}$

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	-0.15531	0.06638	0.32685	0.05983*
C2	-0.02851	0.23221	0.35291	0.02275*
C3	0.1869	0.25126	0.26327	0.02275*
C4	0.24628	0.42934	0.33775	0.02275*
C5	0.4347	0.52818	0.26817	0.05983*
C6	0.118	0.34833	0.12921	0.05983*
H7	0.00819	0.21576	0.46276	0.02058*

H8	-0.13090	0.38187	0.34466	0.02958*
H9	0.28351	0.37630	0.44379	0.02958*
H10	0.10450	0.54936	0.35301	0.02958*
O11	-0.30929	0.02453	0.41739	0.05983*
O12	-0.10754	-0.03339	0.21622	0.05983*
O13	0.53582	0.66706	0.29883	0.05983*
O14	0.54742	0.43056	0.16909	0.05983*
O15	0.00612	0.52016	0.14052	0.05983*
O16	0.2083	0.21459	0.0417	0.05983*
O17	0.32695	0.07281	0.22514	0.05983*
H18	0.394	0.1785	0.2331	0.06878*
K19	0.74052	0.18609	-0.02971	0.04605*
Li20	0.74351	0.74584	0.16276	0.05*
Li21	0.55124	0.10113	0.63762	0.05*

Geometric parameters (Å, °)

C1—C2	1.5101	O15—K19 ⁱ	3.5935
C1—O11	1.2736	O15—K19 ^v	2.7841
C1—O12	1.2730	O15—Li20 ⁱ	2.1241
C2—C1	1.5101	O16—C6	1.2859
C2—C3	1.5407	O16—K19 ⁱ	3.2514
C3—C2	1.5407	O16—K19	3.3912
C3—C4	1.5404	O16—K19 ⁱⁱⁱ	2.6637
C3—C6	1.5507	O16—Li20 ^v	1.9919
C3—O17	1.4328	O17—C3	1.4328
C4—C3	1.5404	O17—K19	3.4878
C4—C5	1.5099	O17—K19 ⁱⁱⁱ	2.7561
C5—C4	1.5099	O17—Li21 ^{vii}	1.9464
C5—O13	1.2711	K19—O12 ^{viii}	3.0147
C5—O14	1.2695	K19—O12 ⁱⁱⁱ	2.8647
C6—C3	1.5507	K19—O13 ^v	3.4733
C6—O15	1.2813	K19—O14	2.6496
C6—O16	1.2859	K19—O14 ^v	3.3644
O11—C1	1.2736	K19—O15 ^{viii}	3.5935
O11—Li21 ⁱ	2.2575	K19—O15 ^v	2.7841
O11—Li21 ⁱⁱ	2.0220	K19—O16	3.3912
O12—C1	1.2730	K19—O16 ^{viii}	3.2514
O12—K19 ⁱ	3.0147	K19—O16 ⁱⁱⁱ	2.6637
O12—K19 ⁱⁱⁱ	2.8647	K19—O17	3.4878
O12—Li20 ^{iv}	1.9891	K19—O17 ⁱⁱⁱ	2.7561
O13—C5	1.2711	Li20—O12 ^{ix}	1.9891
O13—K19 ^v	3.4733	Li20—O13	1.8439
O13—Li20	1.8439	Li20—O14	2.582
O13—Li21 ^{vi}	1.6920	Li20—O15 ^{viii}	2.1241
O14—C5	1.2695	Li20—O16 ^v	1.9919
O14—O13	2.0573	Li21—O11 ^{viii}	2.2575
O14—K19	2.6496	Li21—O11 ⁱⁱ	2.0220

O14—K19 ^v	3.3644	Li21—O13 ^{vi}	1.6920
O14—Li20	2.582	Li21—O17 ^{vii}	1.9464
O15—C6	1.2813		
C2—C1—O11	119.5504	C3—O17—H18	67.1832
C2—C1—O12	120.5205	C3—O17—K19 ⁱⁱⁱ	122.505
O11—C1—O12	119.9213	C3—O17—Li21 ^{vii}	121.6382
C1—C2—C3	120.0207	H18—O17—K19 ⁱⁱⁱ	140.8897
C2—C3—C4	97.8299	H18—O17—Li21 ^{vii}	97.505
C2—C3—C6	100.9126	K19 ⁱⁱⁱ —O17—Li21 ^{vii}	104.7899
C2—C3—O17	119.4522	O12 ^{viii} —K19—O12 ⁱⁱⁱ	93.0913
C4—C3—C6	103.978	O12 ^{viii} —K19—O14	80.1974
C4—C3—O17	124.1292	O12 ^{viii} —K19—O15 ^v	112.4929
C6—C3—O17	107.4222	O12 ^{viii} —K19—O16 ^{viii}	58.136
C3—C4—C5	116.8773	O12 ^{viii} —K19—O16 ⁱⁱⁱ	64.5695
C4—C5—O13	135.3652	O12 ^{viii} —K19—O17 ⁱⁱⁱ	112.5733
C4—C5—O14	114.8354	O12 ⁱⁱⁱ —K19—O14	151.5549
O13—C5—O14	108.1461	O12 ⁱⁱⁱ —K19—O15 ^v	66.0201
C3—C6—O15	116.7212	O12 ⁱⁱⁱ —K19—O16 ^{viii}	59.37
C3—C6—O16	99.9634	O12 ⁱⁱⁱ —K19—O16 ⁱⁱⁱ	66.8873
O15—C6—O16	143.2807	O12 ⁱⁱⁱ —K19—O17 ⁱⁱⁱ	64.5387
C1—O11—Li21 ⁱ	138.7284	O14—K19—O15 ^v	90.893
C1—O11—Li21 ⁱⁱ	120.5833	O14—K19—O16 ^{viii}	94.4416
Li21 ⁱ —O11—Li21 ⁱⁱ	99.3848	O14—K19—O16 ⁱⁱⁱ	131.1798
C1—O12—K19 ⁱ	113.4217	O14—K19—O17 ⁱⁱⁱ	143.4371
C1—O12—K19 ⁱⁱⁱ	139.176	O15 ^v —K19—O16 ^{viii}	56.1366
C1—O12—Li20 ^{iv}	126.3908	O15 ^v —K19—O16 ⁱⁱⁱ	132.5368
K19 ⁱ —O12—K19 ⁱⁱⁱ	86.9087	O15 ^v —K19—O17 ⁱⁱⁱ	112.9108
K19 ⁱ —O12—Li20 ^{iv}	83.8856	O16 ^{viii} —K19—O16 ⁱⁱⁱ	94.3136
K19 ⁱⁱⁱ —O12—Li20 ^{iv}	89.1605	O16 ^{viii} —K19—O17 ⁱⁱⁱ	121.6786
C5—O13—Li20	116.3317	O16 ⁱⁱⁱ —K19—O17 ⁱⁱⁱ	48.0157
C5—O13—Li21 ^{vi}	130.5031	O12 ^{ix} —Li20—O13	114.3245
Li20—O13—Li21 ^{vi}	96.8988	O12 ^{ix} —Li20—O15 ^{viii}	96.8417
C5—O14—K19	171.2327	O12 ^{ix} —Li20—O16 ^v	99.9031
C6—O15—K19 ^v	108.1884	O13—Li20—O15 ^{viii}	109.5957
C6—O15—Li20 ⁱ	161.8601	O13—Li20—O16 ^v	138.1587
K19 ^v —O15—Li20 ⁱ	88.7083	O15 ^{viii} —Li20—O16 ^v	88.3426
C6—O16—K19 ⁱ	85.8733	O11 ^{viii} —Li21—O11 ⁱⁱ	80.6152
C6—O16—K19 ⁱⁱⁱ	137.0461	O11 ^{viii} —Li21—O13 ^{vi}	127.2048
C6—O16—Li20 ^v	125.4341	O11 ^{viii} —Li21—O17 ^{vii}	113.934
K19 ⁱ —O16—K19 ⁱⁱⁱ	85.6864	O11 ⁱⁱ —Li21—O13 ^{vi}	109.7009
K19 ⁱ —O16—Li20 ^v	78.6777	O11 ⁱⁱ —Li21—O17 ^{vii}	109.0825
K19 ⁱⁱⁱ —O16—Li20 ^v	93.8091	O13 ^{vi} —Li21—O17 ^{vii}	110.782

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

(kadu1697_DFT)

*Crystal data*C₆H₇K₂LiO₈ $M_r = 292.25$ Orthorhombic, *Pmn*2₁

Hall symbol: P 2ac -2

 $a = 10.2488 \text{ \AA}$ $b = 5.8658 \text{ \AA}$ $c = 8.1929 \text{ \AA}$ $V = 492.53 \text{ \AA}^3$ $Z = 2$ *Data collection* $h = \rightarrow$ $l = \rightarrow$ $k = \rightarrow$ *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	0.25085	0.55039	0.91138	0.01550*
C2	0.12106	0.61656	0.83349	0.01010*
H7	0.12406	0.56332	0.70555	0.01310*
H8	0.10941	0.80147	0.83534	0.01310*
O11	0.27114	0.34238	0.94262	0.01550*
O12	0.33128	0.71110	0.93752	0.01550*
K19	0.19597	-0.04778	1.18244	0.03330*
H22	0.42322	0.21715	0.95731	0.04000*
C3	0.00000	0.51342	0.91548	0.01010*
C6	0.00000	0.25095	0.89891	0.01550*
O15	0.00000	0.16665	0.75711	0.01550*
O16	0.00000	0.14035	1.03069	0.01550*
O17	0.00000	0.57368	1.08543	0.01550*
H18	0.00000	0.42546	1.14047	0.02010*
Li20	0.00000	0.19424	0.52218	0.04000*
O21	0.50000	0.11887	0.94174	0.01800*

Bond lengths (\AA)

C1—C2	1.525	C3—C6	1.546
C1—O11	1.264	C3—O17	1.437
C1—O12	1.270	C6—O15	1.263
C2—C3	1.535	C6—O16	1.260
C2—H7	1.094	O15—Li20	1.932
C2—H8	1.091	O16—K19 ^{vii}	2.607
O11—K19 ⁱ	2.765	O17—H18	0.979
O12—K19 ⁱⁱ	2.889	O17—K19 ⁱⁱⁱ	3.098
O12—K19 ⁱⁱⁱ	2.820	O17—K19 ^{viii}	3.098
O12—Li20 ^{iv}	1.944	Li20—O12 ⁱⁱ	1.944
K19—O12 ^{iv}	2.889	Li20—O12 ^{ix}	1.944
K19—O16	2.607	Li20—O21 ⁱ	1.951
K19—O11 ^v	2.765	O21—Li20 ^v	1.951
K19—O17 ^{vi}	3.098	O21—K19 ⁱ	2.953
K19—O12 ^{vi}	2.820	O21—K19 ^x	2.953

K19—O21 ^v	2.953	O21—H22	0.984
H22—O21 ⁱⁱ	0.984	O21—H22 ^{xi}	0.984
C3—C2 ^{vii}	1.535		

Symmetry codes: (i) $-x+1/2, -y, z-1/2$; (ii) $-x+1/2, -y+1, z-1/2$; (iii) $x, y+1, z$; (iv) $-x+1/2, -y+1, z+1/2$; (v) $-x+1/2, -y, z+1/2$; (vi) $x, y-1, z$; (vii) $-x, y, z$; (viii) $-x, y+1, z$; (ix) $x-1/2, -y+1, z-1/2$; (x) $x+1/2, -y, z-1/2$; (xi) $-x+1, y, z$.

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O21—H22...O11	0.98	1.73	2.687	164
O17—H18...O16	0.98	1.90	2.581	124
C2—H7...O11 ⁱⁱ	1.09	2.47	3.396	142

Symmetry code: (ii) $-x+1/2, -y+1, z-1/2$.