

Sodium rubidium hydrogen citrate, $\text{NaRbHC}_6\text{H}_5\text{O}_7$, and sodium caesium hydrogen citrate, $\text{NaCsHC}_6\text{H}_5\text{O}_7$: crystal structures and DFT comparisons

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Received 23 November 2018

Accepted 12 January 2019

Edited by A. Van der Lee, Université de Montpellier II, France

Keywords: powder diffraction; density functional theory; citrate; sodium; rubidium; caesium; crystal structure.

CCDC references: 1890745; 1890746; 1890747; 1890748

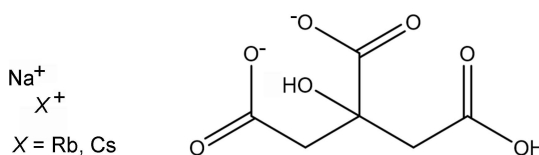
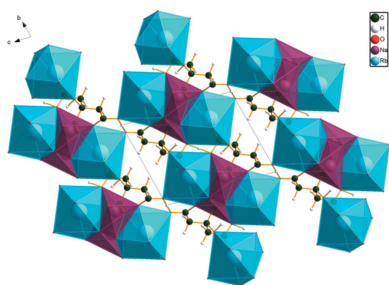
Supporting information: this article has supporting information at journals.iucr.org/e

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The crystal structure of sodium rubidium hydrogen citrate, $\text{NaRbHC}_6\text{H}_5\text{O}_7$ or $[\text{NaRb}(\text{C}_6\text{H}_5\text{O}_7)]_n$, has been solved and refined using laboratory powder X-ray diffraction data, and optimized using density functional techniques. This compound is isostructural to $\text{NaKHC}_6\text{H}_5\text{O}_7$. The Na atom is six-coordinate, with a bond-valence sum of 1.16. The Rb atom is eight-coordinate, with a bond-valence sum of 1.17. The distorted $[\text{NaO}_6]$ octahedra share edges to form chains along the *a*-axis direction. The irregular $[\text{RbO}_8]$ coordination polyhedra share edges with the $[\text{NaO}_6]$ octahedra on either side of the chain, and share corners with other Rb atoms, resulting in triple chains along the *a*-axis direction. The most prominent feature of the structure is the chain along $[111]$ of very short, very strong hydrogen bonds; the $\text{O}\cdots\text{O}$ distances are 2.426 and 2.398 Å. The Mulliken overlap populations in these hydrogen bonds are 0.140 and 0.143 electrons, which correspond to hydrogen-bond energies of about $20.3 \text{ kcal mol}^{-1}$. The crystal structure of sodium caesium hydrogen citrate, $\text{NaCsHC}_6\text{H}_5\text{O}_7$ or $[\text{NaCs}(\text{C}_6\text{H}_5\text{O}_7)]_n$, has also been solved and refined using laboratory powder X-ray diffraction data, and optimized using density functional techniques. The Na atom is six-coordinate, with a bond-valence sum of 1.15. The Cs atom is eight-coordinate, with a bond-valence sum of 0.97. The distorted trigonal-prismatic $[\text{NaO}_6]$ coordination polyhedra share edges to form zigzag chains along the *b*-axis direction. The irregular $[\text{CsO}_8]$ coordination polyhedra share edges with the $[\text{NaO}_6]$ polyhedra to form layers parallel to the (101) plane, unlike the isolated chains in $\text{NaKHC}_6\text{H}_5\text{O}_7$ and $\text{NaRbHC}_6\text{H}_5\text{O}_7$. A prominent feature of the structure is the chain along $[100]$ of very short, very strong $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds; the refined $\text{O}\cdots\text{O}$ distances are 2.398 and 2.159 Å, and the optimized distances are 2.398 and 2.347 Å. The Mulliken overlap populations in these hydrogen bonds are 0.143 and 0.133 electrons, which correspond to hydrogen-bond energies about $20.3 \text{ kcal mol}^{-1}$.

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 metal hydrogen citrates in Cigler & Kaduk (2018). The two title compounds (Figs. 1 and 2) are a further extension to citrates that contain more than one alkali metal cation.



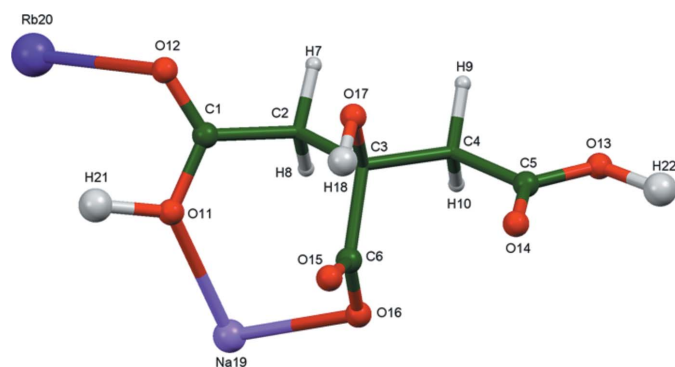


Figure 1
The asymmetric unit of $\text{NaRbHC}_6\text{H}_5\text{O}_7$, with the atom numbering and 50% probability spheroids.

2. Structural commentary

Sodium rubidium hydrogen citrate is isostructural to $\text{NaKHC}_6\text{H}_5\text{O}_7$ (Rammohan & Kaduk, 2016). Sodium caesium hydrogen citrate has a related but different structure. The root-mean-square deviations of the non-hydrogen atoms in the refined and optimized structures are 0.116 and 0.105 Å for $\text{NaRbHC}_6\text{H}_5\text{O}_7$ and $\text{NaCsHC}_6\text{H}_5\text{O}_7$, respectively. Comparisons of the refined and optimized structures are given in Figs. 3 and 4. The excellent agreement between the structures is strong evidence that the experimental structures are correct (van de Streek & Neumann, 2014). This discussion uses the DFT-optimized structures. 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.*, 2008). The citrate anion in both structures occurs in the *trans,trans*-conformation (about C2–C3 and C3–C4), which is one of the two low-energy conformations of an isolated citrate (Rammohan & Kaduk, 2018). The central carboxylate group and the hydroxy group occur in the normal planar arrangement.

In the Rb compound, the citrate chelates to Na19 through the terminal carboxylate oxygen O11 and the central carboxylate oxygen O16. The Na^+ cation is six-coordinate,

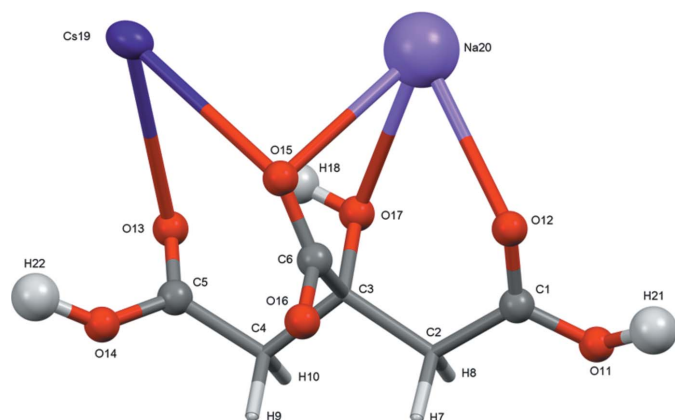


Figure 2
The asymmetric unit of $\text{NaCsHC}_6\text{H}_5\text{O}_7$, with the atom numbering and 50% probability spheroids.

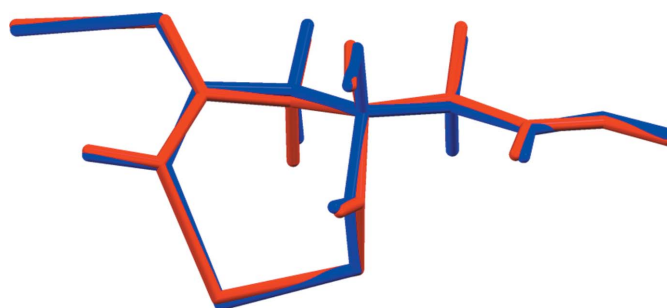


Figure 3
Comparison of the refined and optimized structures of sodium rubidium hydrogen citrate. The refined structure is in red, and the DFT-optimized structure is in blue.

with a bond-valence sum of 1.16. The Rb^+ cation is eight-coordinate, with a bond-valence sum of 1.17. Both cations are thus slightly crowded.

In the Cs compound, the citrate triply chelates to Na20 through the terminal carboxylate oxygen O12, the central carboxylate oxygen O15, and the hydroxyl oxygen O17. The Na^+ cation is six-coordinate, with a bond-valence sum of 1.15. The Cs^+ cation is eight-coordinate, with a bond-valence sum of 0.97. The Rb–O and Cs–O bonds are ionic, but the Na–O bonds have slight covalent character, according to the Mulliken overlap populations.

The Bravais–Friedel–Donnay–Harker (Bravais, 1866; Friedel, 1907; Donnay & Harker, 1937) method suggests that we might expect a platy morphology for $\text{NaRbHC}_6\text{H}_5\text{O}_7$, with {001} as the principal faces, and an elongated morphology for $\text{NaCsHC}_6\text{H}_5\text{O}_7$, with {010} as the long axis. Fourth-order spherical harmonic preferred orientation models were included in the refinements; the texture indices were 1.050 and 1.011, indicating that preferred orientation was slight for the rotated flat-plate specimen of $\text{NaRbHC}_6\text{H}_5\text{O}_7$, but not significant in this rotated capillary specimen of $\text{NaCsHC}_6\text{H}_5\text{O}_7$. Examination of the products under an optical microscope indicated that the morphologies were not especially anisotropic.

3. Supramolecular features

In the crystal structure of $\text{NaRbHC}_6\text{H}_5\text{O}_7$ (Fig. 5), distorted $[\text{NaO}_6]$ octahedra share edges to form chains along the *a*-axis direction. The irregular $[\text{RbO}_8]$ coordination polyhedra share

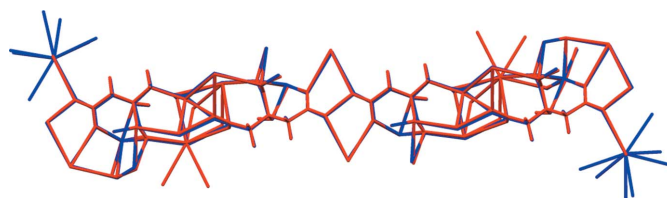


Figure 4
Comparison of the refined and optimized structures of sodium caesium hydrogen citrate. The refined structure is in red, and the DFT-optimized structure is in blue.

Table 1
Hydrogen-bond geometry for [NaRb(C₆H₆O₇)].

<i>D</i> –H··· <i>A</i>	<i>D</i> –H (Å)	H··· <i>A</i> (Å)	<i>D</i> ··· <i>A</i> (Å)	<i>D</i> –H··· <i>A</i> (°)	Mulliken overlap (electrons)	H-bond energy (kcal mol ⁻¹)
O13–H22···O13 ⁱ	1.199	1.199	2.398	180.0	0.143	20.7
O11–H21···O11 ⁱⁱ	1.213	1.213	2.426	180.0	0.140	20.5
O17–H18···O15	0.979	1.873	2.575	126.2	0.059	13.3
O17–H18···O11 ⁱⁱⁱ	0.979	2.507	3.180	125.8	0.016	6.9
C2–H8···O14 ^{iv}	1.094	2.478	3.541	163.7	0.018	

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

Table 2
Hydrogen-bond geometry for [NaCs(C₆H₆O₇)].

<i>D</i> –H··· <i>A</i>	<i>D</i> –H (Å)	H··· <i>A</i> (Å)	<i>D</i> ··· <i>A</i> (Å)	<i>D</i> –H··· <i>A</i> (°)	Mulliken overlap (electrons)	H-bond energy (kcal mol ⁻¹)
O14–H22···O14 ⁱ	1.200	1.200	2.347	156.1	0.133	19.9
O11–H21···O11 ⁱⁱ	1.203	1.203	2.398	170.6	0.143	20.7
O17–H18···O13 ¹¹¹	0.976	1.941	2.779	142.4	0.046	11.7

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

edges with the [NaO₆] octahedra on either side of the chain, resulting in triple chains along the *a*-axis direction. The most prominent feature of the structure is the chain along [111] of very short, very strong O–H···O hydrogen bonds (Table 1); the refined O···O distances are 2.180 (9) and 2.234 (20) Å, and the optimized distances are 2.426 and 2.398 Å. The Mulliken overlap populations in these hydrogen bonds are 0.140 and 0.143 electrons, which correspond to hydrogen-bond energies about 20.6 kcal mol⁻¹, according to the correlation in Rammohan & Kaduk (2018). H18 forms bifurcated hydrogen bonds: one is intramolecular to O15, and the other is intermolecular to O11.

In the crystal structure of NaCsHC₆H₅O₇ (Fig. 6), distorted trigonal–prismatic [NaO₆] share edges to form zigzag chains along the *b*-axis direction. The irregular [CsO₈] coordination polyhedra share edges with the [NaO₆] polyhedra to form layers parallel to the (101) plane, unlike the isolated chains in NaKHC₆H₅O₇ and NaRbHC₆H₅O₇. A prominent feature of

the structure is the chain along [100] of very short, and very strong O–H···O hydrogen bonds (Table 2); the refined O11···O11 and O14···O14 distances are 2.398 and 2.159 Å, and the optimized distances are 2.398 and 2.347 Å. The Mulliken overlap populations in these hydrogen bonds are 0.143 and 0.133 electrons, which correspond to hydrogen-bond energies about 20.3 kcal mol⁻¹. H18 forms an intramolecular hydrogen bond to O13, one of the terminal carboxylate oxygen atoms.

4. Database survey

Details of the comprehensive literature search for citrate structures are presented in Rammohan & Kaduk (2018). After manually locating the peaks in the pattern of NaRbHC₆H₅O₇,

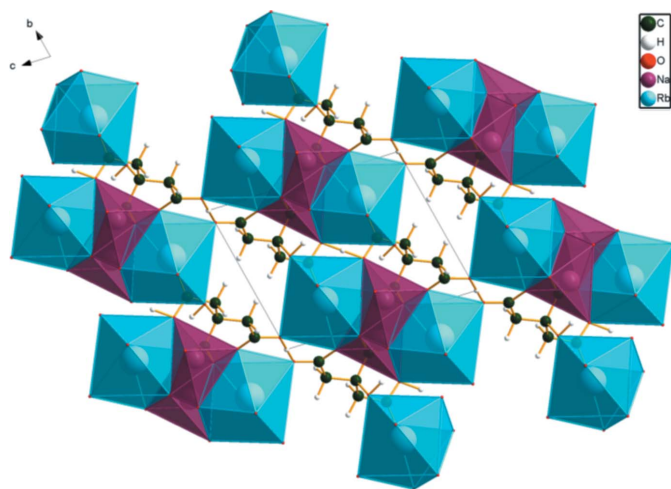


Figure 5
Crystal structure of NaRbHC₆H₅O₇, viewed down the *a* axis.

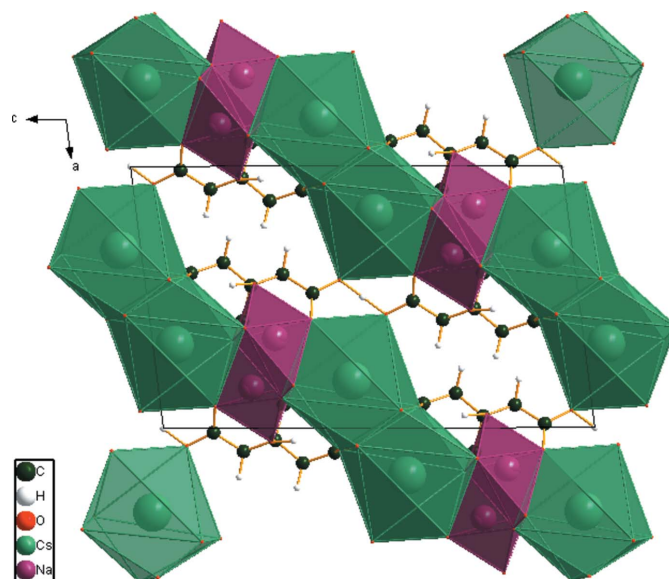


Figure 6
Crystal structure of NaCsHC₆H₅O₇, viewed down the *b* axis.

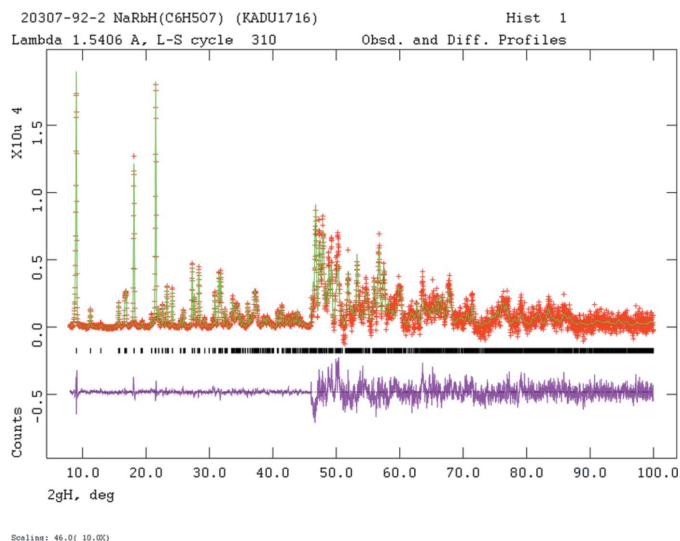


Figure 7
Rietveld plot for $\text{NaRbHC}_6\text{H}_5\text{O}_7$. The red crosses represent the observed data points, and the green line is the calculated pattern. The magenta curve is the difference pattern, plotted at the same scale as the other patterns. The vertical scale has been multiplied by a factor of 10 for $2\theta > 46.0^\circ$. The row of black tick marks indicates the reflection positions for this phase.

the pattern was indexed using *Jade9.8* (MDI, 2017). A reduced-cell search in the Cambridge Structural Database (CSD Version 5.39, update of November 2018; Groom *et al.*, 2016) yielded 39 hits, among which was $\text{NaKHC}_6\text{H}_5\text{O}_7$ (Rammohan & Kaduk, 2016).

After manually locating the peaks in the pattern of $\text{NaCsHC}_6\text{H}_5\text{O}_7$, the pattern was indexed on a *C*-centered monoclinic cell using *Jade9.8* (MDI, 2017). A reduced-cell search in the CSD yielded no hits. The cell was converted to *I*-centered, to yield a β angle closer to 90° .

5. Synthesis and crystallization

Stoichiometric quantities of Na_2CO_3 and Rb_2CO_3 were added to a solution of 10.0 mmol citric acid monohydrate in 10 mL water. After the fizzing subsided, the clear solution was dried in an oven at 403 K to yield the white solid $\text{NaRbHC}_6\text{H}_5\text{O}_7$.

2.0236 g (10.0 mmol) of $\text{H}_3\text{C}_6\text{H}_5\text{O}_7(\text{H}_2\text{O})$ were dissolved in 10 mL of deionized water. 0.5318 g of Na_2CO_3 (1.0 mmol Na, Sigma–Aldrich) and 1.6911 g of Cs_2CO_3 (10.0 mmol of Ca, Sigma–Aldrich) were added to the citric acid solution slowly with stirring. The resulting clear colorless solution was evaporated to dryness in a 403 K oven to yield $\text{NaCsHC}_6\text{H}_5\text{O}_7$.

6. Refinement

The initial structural model for $\text{NaRbHC}_6\text{H}_5\text{O}_7$ was taken from Rammohan & Kaduk (2016), replacing the K by Rb and changing the lattice parameters to the observed values. Pseudovoigt profile coefficients were as parameterized in Thompson *et al.* (1987) and the asymmetry correction of Finger *et al.* (1994) was applied as well as the microstrain

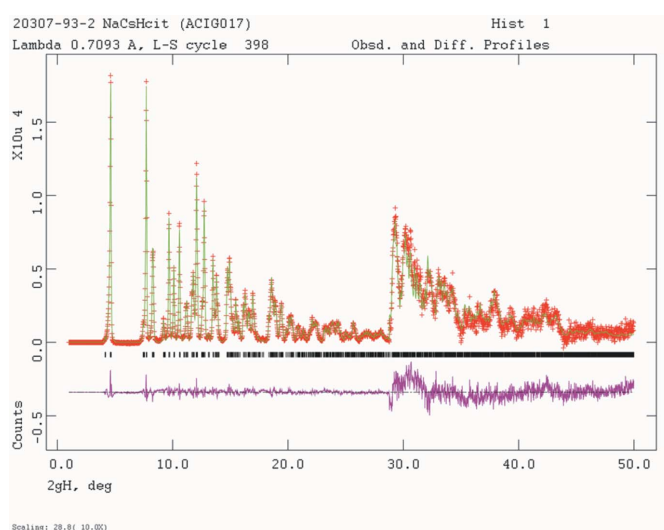


Figure 8
Rietveld plot for $\text{NaCsHC}_6\text{H}_5\text{O}_7$. The red crosses represent the observed data points, and the green line is the calculated pattern. The magenta curve is the difference pattern, plotted at the same scale as the other patterns. The vertical scale has been multiplied by a factor of 10 for $2\theta > 28.8^\circ$. The row of black tick marks indicates the reflection positions for this phase.

broadening description by Stephens (1999). The hydrogen atoms were included in fixed positions, which were re-calculated during the course of the refinement. Crystal data, data collection and structure refinement (Fig. 7) details are summarized in Table 3. The U_{iso} of C2, C3, and C4 were constrained to be equal, and those of H7, H8, H9, and H10 were constrained to be $1.3 \times$ 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 $1.3 \times$ this value. The U_{iso} of H21 and H22 were fixed.

Analysis of the systematic absences in the pattern of $\text{NaCsHC}_6\text{H}_5\text{O}_7$ suggested the space groups *I2*, *Im*, or *I2/m*. The volume of the unit cell corresponded to $Z = 4$. Space group *I2* was selected, and confirmed by successful solution and refinement of the structure. The structure was solved with *FOX* (Favre-Nicolin & Černý, 2002). The maximum $\sin \theta/\lambda$ used for structure solution was 0.55 Å, and a citrate, Cs, Na, and O (water molecule) were used as fragments. The solution with the lowest cost factor has the Cs, Na, and O on top of each other, but the Cs was eight-coordinate and all six carboxylate oxygen atoms were coordinated to the Cs atom. The structure was examined for voids using *Materials Studio* (Dassault Systemes, 2017). One void at approximately 0.375,0.600,0.379 had acceptable coordination to O atoms, and was assigned as Na20. Another void was assigned as O21, but this moved too close to the citrate anion on refinement and was discarded. Active hydrogen atoms were placed by analysis of hydrogen-bonding interactions. The refinement strategy (Fig. 8) was similar to that used for the Rb compound. Cs19 was refined anisotropically.

Density functional geometry optimizations (fixed experimental unit cells) were carried out using *CRYSTAL14* (Dovesi *et al.*, 2014). The basis sets for the H, C, and O atoms

Table 3
Experimental details.

	[NaRb(C ₆ H ₆ O ₇)]	[NaCs(C ₆ H ₆ O ₇)]
Crystal data		
M_r	298.57	346.00
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $I2$
Temperature (K)	300	300
a, b, c (Å)	5.9864 (2), 8.4104 (3), 10.2903 (3)	10.8913 (5), 5.5168 (2), 17.7908 (8)
α, β, γ (°)	74.798 (3), 76.756 (3), 72.878 (2)	90, 97.014 (4), 90
V (Å ³)	471.28 (3)	1060.96 (6)
Z	2	4
Radiation type	$K\alpha_1, K\alpha_2, \lambda = 1.540593, 1.544451$ Å	$K\alpha_1, K\alpha_2, \lambda = 0.709319, 0.713609$ Å
μ (mm ⁻¹)	–	2.09
Specimen shape, size (mm)	Flat sheet, 24 × 24	Cylinder, 12 × 0.3
Data collection		
Diffractometer	Bruker D2 Phaser	PANalytical Empyrean
Specimen mounting	Standard holder	Glass capillary
Data collection mode	Reflection	Transmission
Scan method	Step	Step
2θ values (°)	$2\theta_{\min} = 5.001$ $2\theta_{\max} = 100.007$ $2\theta_{\text{step}} = 0.020$	$2\theta_{\min} = 1.011$ $2\theta_{\max} = 49.991$ $2\theta_{\text{step}} = 0.017$
Refinement		
R factors and goodness of fit	$R_p = 0.028, R_{wp} = 0.038, R_{exp} = 0.022,$ $R(F^2) = 0.13613, \chi^2 = 3.028$	$R_p = 0.045, R_{wp} = 0.059, R_{exp} = 0.026,$ $R(F^2) = 0.08622, \chi^2 = 5.570$
No. of parameters	84	80
No. of restraints	29	29
H-atom treatment	Only H-atom displacement parameters refined	Only H-atom displacement parameters refined

The same symmetry and lattice parameters were used for the DFT calculations as for each powder diffraction study. Computer programs: *DIFFRAC.Measurement* (Bruker, 2009), *FOX* (Favre-Nicolin & Černý, 2002), *GSAS* (Larson & Von Dreele, 2004), *Mercury* (Macrae *et al.*, 2008), *DIAMOND* (Crystal Impact, 2015) and *publCIF* (Westrip, 2010).

were those of Gatti *et al.* (1994), the basis sets for Na was that of Dovesi *et al.* (1991), and the basis sets for Rb and Cs were those of Sophia *et al.* (2014). The calculations were run on eight 2.1 GHz Xeon cores (each with 6 GB RAM) of a 304-core Dell Linux cluster at Illinois Institute of Technology, using 8 k -points and the B3LYP functional, and took 10.8 and 7.5 h.

Acknowledgements

We thank Andrey Rogachev for the use of computing resources at the Illinois Institute of Technology.

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supporting information

Acta Cryst. (2019). E75, 223-227 [https://doi.org/10.1107/S205698901900063X]

Sodium rubidium hydrogen citrate, NaRbHC₆H₅O₇, and sodium caesium hydrogen citrate, NaCsHC₆H₅O₇: crystal structures and DFT comparisons

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Computing details

Data collection: *DIFFRAC.Measurement* (Bruker, 2009) for KADU1716_publ, ACIG017_publ. Program(s) used to solve structure: *FOX* (Favre-Nicolin & Černý, 2002) for KADU1716_publ, ACIG017_publ. Program(s) used to refine structure: *GSAS* (Larson & Von Dreele, 2004) for KADU1716_publ, ACIG017_publ. Molecular graphics: *Mercury* (Macrae *et al.*, 2008), *DIAMOND* (Crystal Impact, 2015) for KADU1716_publ, ACIG017_publ. Software used to prepare material for publication: *publCIF* (Westrip, 2010) for KADU1716_publ, ACIG017_publ.

Poly[(μ -hydrogen citrato)rubidiumsodium] (KADU1716_publ)

Crystal data

[NaRb(C₆H₅O₇)]
 $M_r = 298.57$
Triclinic, $P\bar{1}$
Hall symbol: -P 1
 $a = 5.9864$ (2) Å
 $b = 8.4104$ (3) Å
 $c = 10.2903$ (3) Å
 $\alpha = 74.798$ (3)°
 $\beta = 76.756$ (3)°
 $\gamma = 72.878$ (2)°

$V = 471.28$ (3) Å³
 $Z = 2$
 $D_x = 2.104$ Mg m⁻³
K α_1 , K α_2 radiation, $\lambda = 1.540593, 1.544451$ Å
 $T = 300$ K
Particle morphology: powder
white
flat_sheet, 24 × 24 mm
Specimen preparation: Prepared at 403 K

Data collection

Bruker D2 Phaser
diffractometer
Radiation source: sealed X-ray tube
Specimen mounting: standard holder

Data collection mode: reflection
Scan method: step
 $2\theta_{\min} = 5.001^\circ$, $2\theta_{\max} = 100.007^\circ$, $2\theta_{\text{step}} = 0.020^\circ$

Refinement

Least-squares matrix: full
 $R_p = 0.028$
 $R_{\text{wp}} = 0.038$
 $R_{\text{exp}} = 0.022$
 $R(F^2) = 0.13613$
4701 data points

Profile function: CW Profile function number 4
 with 27 terms Pseudovoigt profile coefficients
 as parameterized in P. Thompson, D.E. Cox &
 J.B. Hastings (1987). J. Appl. Cryst.,20,79-83.
 Asymmetry correction of L.W. Finger, D.E. Cox
 & A. P. Jephcoat (1994). J. Appl.
 Cryst.,27,892-900. Microstrain broadening by
 P.W. Stephens, (1999). J. Appl.
 Cryst.,32,281-289. #1(GU) = 2.580 #2(GV) =
 0.000 #3(GW) = 1.999 #4(GP) = 0.000 #5(LX)
 = 4.181 #6(ptec) = 1.74 #7(trns) = 4.34 #8(shft)
 = -2.5167 #9(sfec) = 0.00 #10(S/L) = 0.0235
 #11(H/L) = 0.0200 #12(eta) = 0.0000 Peak tails
 are ignored where the intensity is below 0.0050
 times the peak Aniso. broadening axis 0.0 0.0
 1.0
 84 parameters
 29 restraints
 2 constraints
 Only H-atom displacement parameters refined
 Weighting scheme based on measured s.u.'s
 $(\Delta/\sigma)_{\max} = 0.03$
 Background function: GSAS Background
 function number 1 with 10 terms. Shifted
 Chebyshev function of 1st kind 1: 1751.95 2:
 -322.287 3: 62.9433 4: -1.65870 5: 15.3537 6:
 -30.8122 7: 27.0452 8: -10.7829 9: 5.15006 10:
 -0.147912

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.592 (2)	0.5051 (13)	0.6742 (10)	0.021 (2)*
C2	0.556 (2)	0.5974 (17)	0.7878 (10)	0.003 (6)*
C3	0.7655 (17)	0.6762 (10)	0.7701 (7)	0.003 (6)*
C4	0.744 (2)	0.7373 (16)	0.9020 (8)	0.003 (6)*
C5	0.905 (3)	0.851 (3)	0.8880 (9)	0.021 (2)*
C6	0.7512 (17)	0.8313 (11)	0.6487 (8)	0.021 (2)*
H7	0.54367	0.50387	0.89029	0.004 (7)*
H8	0.38434	0.70246	0.78480	0.004 (7)*
H9	0.79156	0.62260	0.98785	0.004 (7)*
H10	0.55240	0.80973	0.93127	0.004 (7)*
O11	0.507 (2)	0.5851 (14)	0.5670 (8)	0.021 (2)*
O12	0.657 (3)	0.3441 (14)	0.6967 (12)	0.021 (2)*
O13	0.898 (3)	0.9131 (19)	0.9900 (15)	0.021 (2)*
O14	1.045 (2)	0.8875 (18)	0.7771 (10)	0.021 (2)*
O15	0.914 (3)	0.8275 (16)	0.5451 (11)	0.021 (2)*
O16	0.5597 (18)	0.9458 (15)	0.6434 (12)	0.021 (2)*
O17	0.983 (2)	0.5533 (13)	0.7469 (11)	0.021 (2)*
H18	1.06896	0.61913	0.65793	0.027 (3)*
Na19	0.2740 (17)	0.8715 (12)	0.5586 (9)	0.038 (5)*
Rb20	0.1828 (6)	0.2215 (5)	0.7148 (3)	0.060 (2)*

H21	0.5	0.5	0.5	0.03*
H22	1.0	1.0	1.0	0.03*

Geometric parameters (Å, °)

C1—C2	1.5091 (17)	O14—Rb20 ^{iv}	3.028 (14)
C1—O11	1.261 (3)	O15—C6	1.269 (3)
C1—O12	1.267 (3)	O15—Na19 ⁱⁱ	2.332 (16)
C2—C1	1.5091 (17)	O15—Na19 ^v	2.504 (13)
C2—C3	1.5403 (17)	O15—Rb20 ⁱ	3.013 (16)
C3—C2	1.5403 (17)	O16—C3	2.429 (6)
C3—C4	1.5392 (17)	O16—C6	1.263 (3)
C3—C6	1.5486 (17)	O16—O15	2.193 (8)
C3—O17	1.419 (3)	O16—O16 ^v	3.04 (2)
C4—C3	1.5392 (17)	O16—Na19	2.382 (17)
C4—C5	1.5111 (17)	O16—Na19 ^v	2.439 (13)
C5—C4	1.5111 (17)	O16—Rb20 ^{vi}	2.839 (11)
C5—O13	1.275 (3)	O17—C3	1.419 (3)
C5—O14	1.274 (3)	O17—Rb20 ⁱⁱ	2.769 (10)
C6—C3	1.5486 (17)	Na19—O11	2.393 (16)
C6—O15	1.269 (3)	Na19—O12 ⁱ	3.453 (14)
C6—O16	1.263 (3)	Na19—O14 ^{vii}	2.366 (13)
O11—C1	1.261 (3)	Na19—O15 ^{vii}	2.332 (16)
O11—Na19	2.393 (16)	Na19—O15 ^v	2.504 (13)
O11—Rb20 ⁱ	3.366 (12)	Na19—O16	2.382 (17)
O12—C1	1.267 (3)	Na19—O16 ^v	2.439 (13)
O12—C2	2.411 (8)	Rb20—O11 ⁱ	3.366 (12)
O12—Rb20	3.246 (14)	Rb20—O12 ^{vii}	3.044 (13)
O12—Rb20 ⁱⁱ	3.044 (13)	Rb20—O12	3.246 (14)
O13—C5	1.275 (3)	Rb20—O13 ⁱⁱⁱ	2.931 (16)
O13—Rb20 ⁱⁱⁱ	2.931 (16)	Rb20—O14 ^{viii}	3.028 (14)
O13—H22	1.117 (10)	Rb20—O15 ⁱ	3.013 (16)
O14—C4	2.433 (14)	Rb20—O16 ^{ix}	2.839 (11)
O14—C5	1.274 (3)	Rb20—O17 ^{vii}	2.769 (10)
O14—Na19 ⁱⁱ	2.366 (13)		
C2—C1—O11	118.7 (8)	O11—Na19—O15 ^v	158.0 (5)
C2—C1—O12	120.3 (6)	O11—Na19—O16	92.2 (5)
O11—C1—O12	119.1 (7)	O11—Na19—O16 ^v	108.6 (6)
C1—C2—C3	109.8 (5)	O14 ^{vii} —Na19—O15 ^{vii}	75.6 (5)
C2—C3—C4	107.2 (4)	O14 ^{vii} —Na19—O15 ^v	93.6 (5)
C2—C3—C6	110.0 (4)	O14 ^{vii} —Na19—O16	84.7 (5)
C2—C3—O17	110.1 (5)	O14 ^{vii} —Na19—O16 ^v	140.0 (6)
C4—C3—C6	108.9 (5)	O15 ^{vii} —Na19—O15 ^v	82.9 (6)
C4—C3—O17	110.8 (5)	O15 ^{vii} —Na19—O16	159.9 (7)
C6—C3—O17	109.9 (4)	O15 ^{vii} —Na19—O16 ^v	114.6 (6)
C3—C4—C5	113.0 (7)	O15 ^v —Na19—O16	94.3 (7)
C4—C5—O13	118.6 (6)	O15 ^v —Na19—O16 ^v	52.7 (2)

C4—C5—O14	121.5 (11)	O16—Na19—O16 ^v	78.1 (5)
O13—C5—O14	119.9 (8)	O11 ⁱ —Rb20—O12 ^{vii}	109.5 (3)
C3—C6—O15	119.6 (5)	O11 ⁱ —Rb20—O12	53.0 (3)
C3—C6—O16	119.2 (5)	O11 ⁱ —Rb20—O13 ⁱⁱⁱ	151.0 (3)
O15—C6—O16	120.1 (6)	O11 ⁱ —Rb20—O14 ^{viii}	130.8 (3)
C1—O11—Na19	118.5 (9)	O11 ⁱ —Rb20—O15 ⁱ	67.2 (3)
C1—O11—Rb20 ⁱ	123.9 (10)	O11 ⁱ —Rb20—O16 ^{ix}	77.9 (3)
Na19—O11—Rb20 ⁱ	81.1 (4)	O11 ⁱ —Rb20—O17 ^{vii}	82.2 (3)
C1—O12—Rb20	105.2 (8)	O12 ^{vii} —Rb20—O12	144.3 (4)
C1—O12—Rb20 ⁱⁱ	110.5 (10)	O12 ^{vii} —Rb20—O13 ⁱⁱⁱ	93.8 (4)
Rb20—O12—Rb20 ⁱⁱ	144.3 (4)	O12 ^{vii} —Rb20—O14 ^{viii}	78.6 (3)
C5—O13—Rb20 ⁱⁱⁱ	132.3 (10)	O12 ^{vii} —Rb20—O15 ⁱ	68.6 (3)
C5—O14—Na19 ⁱⁱ	160.1 (13)	O12 ^{vii} —Rb20—O16 ^{ix}	135.6 (4)
C5—O14—Rb20 ^{iv}	118.0 (12)	O12 ^{vii} —Rb20—O17 ^{vii}	66.2 (4)
Na19 ⁱⁱ —O14—Rb20 ^{iv}	81.6 (5)	O12—Rb20—O13 ⁱⁱⁱ	98.0 (3)
C6—O15—Na19 ⁱⁱ	118.8 (12)	O12—Rb20—O14 ^{viii}	137.1 (3)
C6—O15—Na19 ^v	90.6 (6)	O12—Rb20—O15 ⁱ	117.4 (3)
C6—O15—Rb20 ⁱ	119.3 (11)	O12—Rb20—O16 ^{ix}	76.0 (3)
Na19 ⁱⁱ —O15—Na19 ^v	97.1 (6)	O12—Rb20—O17 ^{vii}	79.7 (3)
Na19 ⁱⁱ —O15—Rb20 ⁱ	121.9 (4)	O13 ⁱⁱⁱ —Rb20—O14 ^{viii}	69.3 (3)
Na19 ^v —O15—Rb20 ⁱ	79.8 (4)	O13 ⁱⁱⁱ —Rb20—O15 ⁱ	140.0 (3)
C6—O16—Na19	112.9 (12)	O13 ⁱⁱⁱ —Rb20—O16 ^{ix}	97.6 (4)
C6—O16—Na19 ^v	93.8 (6)	O13 ⁱⁱⁱ —Rb20—O17 ^{vii}	92.2 (4)
C6—O16—Rb20 ^{vi}	158.9 (12)	O14 ^{viii} —Rb20—O15 ⁱ	72.0 (3)
Na19—O16—Na19 ^v	101.9 (5)	O14 ^{viii} —Rb20—O16 ^{ix}	66.0 (4)
Na19—O16—Rb20 ^{vi}	85.5 (4)	O14 ^{viii} —Rb20—O17 ^{vii}	139.1 (4)
Na19 ^v —O16—Rb20 ^{vi}	92.3 (4)	O15 ⁱ —Rb20—O16 ^{ix}	75.4 (4)
O11—Na19—O14 ^{vii}	107.9 (5)	O15 ⁱ —Rb20—O17 ^{vii}	110.9 (4)
O11—Na19—O15 ^{vii}	97.9 (6)	O16 ^{ix} —Rb20—O17 ^{vii}	154.8 (3)

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

(kadu1716_DFT)

Crystal data

$C_6H_6NaO_7Rb$

$M_r = 298.57$

Triclinic, $P\bar{1}$

$a = 5.9859 \text{ \AA}$

$b = 8.4102 \text{ \AA}$

$c = 10.2904 \text{ \AA}$

$\alpha = 74.7995^\circ$

$\beta = 76.7573^\circ$

$\gamma = 72.8749^\circ$

$V = 471.23 \text{ \AA}^3$

$Z = 2$

Data collection

$h = \rightarrow$

$l = \rightarrow$

$k = \rightarrow$

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.58312	0.48855	0.68564	0.01800*

C2	0.57651	0.57925	0.79638	0.00600*
C3	0.76841	0.67872	0.76846	0.00600*
C4	0.73694	0.75315	0.89436	0.00600*
C5	0.90081	0.86416	0.88638	0.01800*
C6	0.74570	0.82427	0.63974	0.01800*
H7	0.60167	0.48235	0.88975	0.00700*
H8	0.40172	0.66683	0.81269	0.00700*
H9	0.76305	0.64923	0.98397	0.00700*
H10	0.55518	0.83019	0.91496	0.00700*
O11	0.50420	0.58854	0.57498	0.01800*
O12	0.65090	0.33239	0.70086	0.01800*
O13	0.87388	0.91272	0.99960	0.01800*
O14	1.04257	0.90330	0.78197	0.01800*
O15	0.91969	0.81409	0.54210	0.01800*
O16	0.56046	0.94323	0.63928	0.01800*
O17	0.99694	0.56509	0.74766	0.01800*
H18	1.06896	0.61913	0.65793	0.02340*
Na19	0.25929	0.87959	0.56024	0.02900*
Rb20	0.19358	0.22247	0.71319	0.05030*
H21	0.50000	0.50000	0.50000	0.03000*
H22	1.00000	1.00000	1.00000	0.03000*

Bond lengths (Å)

C1—C2	1.516	C4—H10	1.095
C1—O11	1.318	C5—O13	1.294
C1—O12	1.233	C5—O14	1.243
C2—C3	1.546	C6—O15	1.271
C2—H7	1.092	C6—O16	1.256
C2—H8	1.094	O11—H21	1.213
C3—C4	1.533	O13—H22	1.199
C3—C6	1.551	O17—H18	0.979
C3—O17	1.426	H21—O11 ⁱ	1.213
C4—C5	1.517	H22—O13 ⁱⁱ	1.199
C4—H9	1.096		

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, -y+2, -z+2$.*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O13—H22 \cdots O13	1.199	1.199	2.398	180.0
O11—H21 \cdots O11	1.213	1.213	2.426	180.0
O17—H18 \cdots O15	0.979	1.873	2.575	126.2
O17—H18 \cdots O11	0.979	2.507	3.180	125.8
C2—H8 \cdots O14	1.094	2.478	3.541	163.7

Poly[(μ -hydrogen citrato)caesiumsodium] (ACIG017_publ)*Crystal data*[CsNa(C₆H₆O₇)] $M_r = 346.00$ Monoclinic, $I2$ Hall symbol: $I\ 2y$ $a = 10.8913\ (5)\ \text{\AA}$ $b = 5.5168\ (2)\ \text{\AA}$ $c = 17.7908\ (8)\ \text{\AA}$ $\beta = 97.014\ (4)^\circ$ $V = 1060.96\ (6)\ \text{\AA}^3$ $Z = 4$ $D_x = 2.166\ \text{Mg m}^{-3}$ $K\alpha_1, K\alpha_2$ radiation, $\lambda = 0.709319, 0.713609\ \text{\AA}$ $\mu = 2.09\ \text{mm}^{-1}$ $T = 300\ \text{K}$

Particle morphology: powder

white

cylinder, $12 \times 0.3\ \text{mm}$

Specimen preparation: Prepared at 403 K

*Data collection*PANalytical Empyrean
diffractometer

Radiation source: sealed X-ray tube

Specimen mounting: glass capillary

Data collection mode: transmission

Scan method: step

 $2\theta_{\min} = 1.011^\circ, 2\theta_{\max} = 49.991^\circ, 2\theta_{\text{step}} = 0.017^\circ$ *Refinement*

Least-squares matrix: full

 $R_p = 0.045$ $R_{\text{wp}} = 0.059$ $R_{\text{exp}} = 0.026$ $R(F^2) = 0.08622$

2932 data points

Profile function: CW Profile function number 4

with 21 terms Pseudovoigt profile coefficients

as parameterized in P. Thompson, D.E. Cox &

J.B. Hastings (1987). *J. Appl. Cryst.*, 20, 79-83.

Asymmetry correction of L.W. Finger, D.E. Cox

& A. P. Jephcoat (1994). *J. Appl.**Cryst.*, 27, 892-900. Microstrain broadening byP.W. Stephens, (1999). *J. Appl.**Cryst.*, 32, 281-289. #1(GU) = 53.860 #2(GV) =

0.000 #3(GW) = 0.786 #4(GP) = 0.000 #5(LX)

= 1.886 #6(ptec) = 0.00 #7(trns) = 0.00 #8(shft)

= 0.0000 #9(sfec) = 0.00 #10(S/L) = 0.0151

#11(H/L) = 0.0173 #12(eta) = 0.5113 #13(S400

) = 1.1E-01 #14(S040) = 4.6E-01 #15(S004) =

6.1E-03 #16(S220) = 2.3E-01 #17(S202) =

3.5E-02 #18(S022) = 7.8E-02 #19(S301) =

8.2E-02 #20(S103) = -1.3E-02 #21(S121) =

7.3E-02 Peak tails are ignored where the

intensity is below 0.0050 times the peak Aniso.

broadening axis 0.0 0.0 1.0

80 parameters

29 restraints

2 constraints

Only H-atom displacement parameters refined

Weighting scheme based on measured s.u.'s

 $(\Delta/\sigma)_{\max} = 0.06$

Background function: GSAS Background

function number 1 with 3 terms. Shifted

Chebyshev function of 1st kind 1: 711.736 2:

51.3623 3: -153.142

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	0.5180 (19)	0.183 (7)	0.3879 (6)	0.027 (3)*
C2	0.5919 (14)	0.118 (3)	0.3242 (6)	0.002 (7)*
C3	0.5465 (10)	0.234 (2)	0.2470 (5)	0.002 (7)*
C4	0.6279 (14)	0.138 (3)	0.1886 (6)	0.002 (7)*
C5	0.588 (2)	0.249 (3)	0.1120 (6)	0.027 (3)*
C6	0.4103 (11)	0.162 (3)	0.2216 (9)	0.027 (3)*
H7	0.58724	-0.0875	0.31719	0.003 (9)*
H8	0.69162	0.17452	0.33886	0.003 (9)*
H9	0.61841	-0.06615	0.18447	0.003 (9)*
H10	0.72772	0.19018	0.20703	0.003 (9)*
O11	0.5625 (17)	0.129 (4)	0.4554 (6)	0.027 (3)*
O12	0.4121 (17)	0.285 (4)	0.3756 (9)	0.027 (3)*
O13	0.601 (3)	0.476 (3)	0.1023 (8)	0.027 (3)*
O14	0.5515 (19)	0.112 (3)	0.0558 (7)	0.027 (3)*
O15	0.3392 (15)	0.319 (3)	0.1871 (10)	0.027 (3)*
O16	0.3821 (15)	-0.062 (3)	0.2172 (12)	0.027 (3)*
O17	0.5558 (14)	0.490 (2)	0.2509 (8)	0.027 (3)*
H18	0.54799	0.56496	0.20157	0.036 (4)*
Cs19	0.3269 (3)	0.70766	0.05362 (15)	0.04276
Na20	0.3483 (18)	0.742 (6)	0.2891 (9)	0.124 (8)*
H21	0.5	0.102	0.5	0.05*
H22	0.5	0.124	0.0	0.05*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cs19	0.039 (3)	0.038 (3)	0.051 (3)	0.006 (5)	0.006 (2)	-0.007 (5)

Geometric parameters (\AA , $^\circ$)

C1—C2	1.512 (2)	O14—Cs19 ^{iv}	3.341 (19)
C1—O11	1.274 (7)	O15—C6	1.272 (7)
C1—O12	1.278 (7)	O15—Cs19	3.189 (17)
C2—C1	1.512 (2)	O15—Na20	2.95 (3)
C2—C3	1.540 (2)	O15—Na20 ⁱ	2.18 (2)
C3—C2	1.540 (2)	O16—C6	1.272 (7)
C3—C4	1.540 (2)	O16—Cs19 ⁱⁱⁱ	3.17 (2)
C3—C6	1.548 (2)	O16—Na20 ⁱⁱⁱ	1.75 (3)
C3—O17	1.419 (7)	O16—Na20 ⁱ	3.01 (3)
C4—C3	1.540 (2)	O17—C3	1.419 (7)
C4—C5	1.509 (2)	O17—Na20	2.81 (3)
C5—C4	1.509 (2)	Cs19—O11 ^v	3.211 (17)
C5—O13	1.272 (7)	Cs19—O12 ^{vi}	3.057 (15)
C5—O14	1.275 (7)	Cs19—O13	3.27 (3)
C6—C3	1.548 (2)	Cs19—O13 ⁱⁱ	3.236 (17)

C6—O15	1.272 (7)	Cs19—O14 ^{vii}	3.309 (17)
C6—O16	1.272 (7)	Cs19—O14 ^{viii}	3.341 (19)
O11—C1	1.274 (7)	Cs19—O15	3.189 (17)
O12—C1	1.278 (7)	Cs19—O16 ^{vii}	3.17 (2)
O12—Cs19 ⁱ	3.057 (15)	Cs19—H18	3.435 (3)
O12—Na20	2.99 (4)	Na20—O12	2.99 (4)
O13—C5	1.272 (7)	Na20—O15	2.95 (3)
O13—Cs19	3.27 (3)	Na20—O15 ^{vi}	2.18 (2)
O13—Cs19 ⁱⁱ	3.236 (17)	Na20—O16 ^{vii}	1.75 (3)
O14—C5	1.275 (7)	Na20—O16 ^{vi}	3.01 (3)
O14—O14 ⁱⁱ	2.16 (3)	Na20—O17	2.81 (3)
O14—Cs19 ⁱⁱⁱ	3.309 (17)		
C2—C1—O11	118.3 (5)	C3—O17—H18	112.6 (12)
C2—C1—O12	121.9 (7)	O11 ^v —Cs19—O12 ^{vi}	59.4 (3)
O11—C1—O12	119.8 (6)	O11 ^v —Cs19—O13	145.2 (5)
C1—C2—C3	115.3 (5)	O11 ^v —Cs19—O13 ⁱⁱ	76.9 (5)
C2—C3—C4	108.1 (6)	O11 ^v —Cs19—O14 ^{vii}	135.3 (5)
C2—C3—C6	110.2 (6)	O11 ^v —Cs19—O14 ^{viii}	99.6 (4)
C2—C3—O17	110.9 (6)	O11 ^v —Cs19—O15	105.5 (4)
C4—C3—C6	108.9 (6)	O11 ^v —Cs19—O16 ^{vii}	127.7 (5)
C4—C3—O17	109.3 (6)	O12 ^{vi} —Cs19—O13	137.9 (6)
C6—C3—O17	109.4 (6)	O12 ^{vi} —Cs19—O13 ⁱⁱ	135.7 (6)
C3—C4—C5	110.0 (6)	O12 ^{vi} —Cs19—O14 ^{vii}	124.5 (5)
C4—C5—O13	119.6 (8)	O12 ^{vi} —Cs19—O14 ^{viii}	124.4 (5)
C4—C5—O14	119.7 (6)	O12 ^{vi} —Cs19—O15	75.3 (5)
O13—C5—O14	120.4 (7)	O12 ^{vi} —Cs19—O16 ^{vii}	68.9 (5)
C3—C6—O15	118.0 (6)	O13—Cs19—O13 ⁱⁱ	76.3 (5)
C3—C6—O16	118.9 (7)	O13—Cs19—O14 ^{vii}	67.1 (4)
O15—C6—O16	120.4 (6)	O13—Cs19—O14 ^{viii}	90.1 (5)
C1—O11—Cs19 ^{ix}	134 (2)	O13—Cs19—O15	65.5 (4)
C1—O12—Cs19 ⁱ	131.6 (15)	O13—Cs19—O16 ^{vii}	81.3 (4)
C5—O13—Cs19	107.5 (19)	O13 ⁱⁱ —Cs19—O14 ^{vii}	91.2 (5)
C5—O13—Cs19 ⁱⁱ	123.3 (10)	O13 ⁱⁱ —Cs19—O14 ^{viii}	67.1 (3)
Cs19—O13—Cs19 ⁱⁱ	85.8 (4)	O13 ⁱⁱ —Cs19—O15	112.4 (5)
C5—O14—Cs19 ⁱⁱⁱ	124.4 (14)	O13 ⁱⁱ —Cs19—O16 ^{vii}	155.3 (6)
C5—O14—Cs19 ^{iv}	138.3 (18)	O14 ^{vii} —Cs19—O14 ^{viii}	37.9 (4)
Cs19 ⁱⁱⁱ —O14—Cs19 ^{iv}	83.5 (4)	O14 ^{vii} —Cs19—O15	118.7 (4)
C6—O15—Cs19	141.8 (14)	O14 ^{vii} —Cs19—O16 ^{vii}	70.2 (4)
C6—O15—Na20 ⁱ	107.7 (14)	O14 ^{viii} —Cs19—O15	154.1 (4)
Cs19—O15—Na20 ⁱ	108.7 (8)	O14 ^{viii} —Cs19—O16 ^{vii}	102.9 (4)
C6—O16—Cs19 ⁱⁱⁱ	117.6 (13)	O15—Cs19—O16 ^{vii}	66.3 (3)
C6—O16—Na20 ⁱⁱⁱ	129 (2)	O15 ^{vi} —Na20—O16 ^{vii}	107.9 (15)
Cs19 ⁱⁱⁱ —O16—Na20 ⁱⁱⁱ	113.1 (11)		

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

(acig017_DFT)

*Crystal data*C₆H₆CsNaO₇ $M_r = 346.0$ Monoclinic, *I*2 $a = 10.8918 \text{ \AA}$ $b = 5.5166 \text{ \AA}$ $c = 17.7909 \text{ \AA}$ $\beta = 97.0160^\circ$ $V = 1060.98 \text{ \AA}^3$ $Z = 4$ *Data collection*

DFT calculation

 $h = \rightarrow$ $k = \rightarrow$ $l = \rightarrow$ *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	0.01539	-0.29133	-0.11491	0.02190*
C2	0.08720	-0.37073	-0.17866	0.00770*
C3	0.04485	-0.25744	-0.25560	0.00770*
C4	-0.36770	0.15585	0.18731	0.00770*
C5	-0.40727	0.26100	0.10948	0.02190*
C6	-0.09031	-0.33701	-0.28568	0.02190*
H7	0.07745	0.43212	-0.18341	0.01000*
H8	0.18550	-0.33438	-0.16183	0.01000*
H9	-0.36925	-0.04136	0.18368	0.01000*
H10	-0.27329	0.21290	0.20759	0.01000*
O11	0.06648	-0.36068	-0.04898	0.02190*
O12	-0.08435	-0.17967	-0.12642	0.02190*
O13	-0.41832	0.48425	0.09987	0.02190*
O14	-0.43234	0.10103	0.05664	0.02190*
O15	0.33500	0.32450	0.18636	0.02190*
O16	0.38339	-0.05889	0.21767	0.02190*
O17	0.05257	-0.00031	-0.24718	0.02190*
H18	0.04799	0.06496	-0.29843	0.02800*
Cs19	0.31925	-0.29064	0.05016	0.04080*
Na20	-0.15569	0.10811	-0.21537	0.10800*
H21	0.00000	-0.34288	0.00000	0.05000*
H22	0.00000	-0.35387	0.50000	0.05000*

Bond lengths (\AA)

C1—C2	1.519	O15—Na20 ^{xii}	2.339
C1—O11	1.293	O16—C6 ^{xii}	1.260
C1—O12	1.244	O16—Cs19	3.240
C2—C3	1.524	O16—Na20 ^{xiii}	2.258
C2—H7 ⁱ	1.095	O16—Na20 ^{vii}	2.641
C2—H8	1.095	O17—H18	0.976
C3—C4 ⁱⁱ	1.551	O17—Na20	2.477
C3—C6	1.566	Cs19—Cs19 ^{vi}	5.517
C3—O17	1.428	Cs19—Cs19 ⁱ	5.517

C4—C3 ⁱⁱⁱ	1.551	Cs19—O15 ⁱ	3.210
C4—C5	1.515	Cs19—O12 ^{vii}	3.100
C4—H9	1.090	Cs19—O13 ^{xiv}	3.143
C4—H10	1.094	Cs19—O14 ^{xv}	3.453
C5—O13	1.247	Cs19—O14 ^{vii}	3.220
C5—O14	1.294	Cs19—O13 ^{xvi}	3.246
C6—O15 ^{iv}	1.267	Cs19—Cs19 ^{xvii}	4.517
C6—O16 ^{iv}	1.260	Cs19—Na20 ^{xiii}	4.184
C6—Na20 ^v	2.785	Cs19—Na20 ^{vii}	4.234
H7—C2 ^{vi}	1.095	Na20—O15 ^{vii}	2.398
O11—Cs19	3.107	Na20—C6 ^{xviii}	2.785
O11—H21	1.203	Na20—Na20 ^{xviii}	3.568
O12—Cs19 ^{vii}	3.100	Na20—Na20 ^v	3.568
O12—Na20	2.308	Na20—O16 ^{xi}	2.258
O13—Cs19 ^{viii}	3.143	Na20—O15 ^{iv}	2.339
O13—Cs19 ^{ix}	3.246	Na20—O16 ^{vii}	2.641
O14—Cs19 ^x	3.453	Na20—Cs19 ^{xi}	4.184
O14—Cs19 ^{vii}	3.220	Na20—Cs19 ^{vii}	4.234
O14—H22 ^{xi}	1.200	H21—O11 ^{vii}	1.203
O15—C6 ^{xii}	1.267	H22—O14 ^{xix}	1.200
O15—Cs19 ^{vi}	3.210	H22—O14 ^{xiii}	1.200
O15—Na20 ^{vii}	2.398		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O14—H22 \cdots O14	1.200	1.200	2.347	156.1
O11—H21 \cdots O11	1.203	1.203	2.398	170.6
O17—H18 \cdots O13	0.976	1.941	2.779	142.4