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Trisodium citrate, $Na_3(C_6H_5O_7)$

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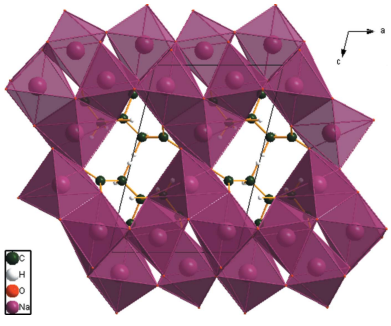
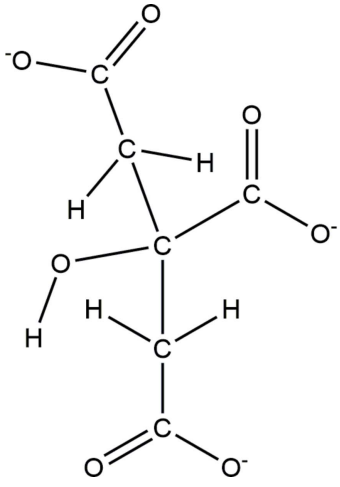
The crystal structure of anhydrous trisodium citrate, $Na_3(C_6H_5O_7)$, has been solved and refined using synchrotron X-ray powder diffraction data, and optimized using density functional theory (DFT). There are two independent five-coordinate Na^+ and one six-coordinate Na^+ cations in the asymmetric unit. The $[NaO_5]$ and $[NaO_6]$ polyhedra share edges and corners to form a three-dimensional framework. There are channels parallel to the *a* and *b* axes in which the remainder of the citrate anions reside. The only hydrogen bonds are an intramolecular one between the hydroxy group and one of the terminal carboxylate O atoms and an intermolecular one between a methylene group and the hydroxyl O atom.

1. Chemical context

In the course of a systematic study of the crystal structures of Group 1 (alkali metal) citrate salts to understand the anion's conformational flexibility, ionization, coordination tendencies, and hydrogen bonding, we have determined several new crystal structures. Most of the new structures were solved using powder diffraction data (laboratory and/or synchrotron), but single crystals were used where available. The general trends and conclusions about the 16 new compounds and 12 previously characterized structures are being reported separately (Rammohan & Kaduk, 2016*a*). Two of the new structures containing multiple Group 1 cations) – $NaKHC_6H_5O_7$ and $NaK_2C_6H_5O_7$ – have been published recently (Rammohan & Kaduk, 2016*b*,*c*).





$3Na^+$

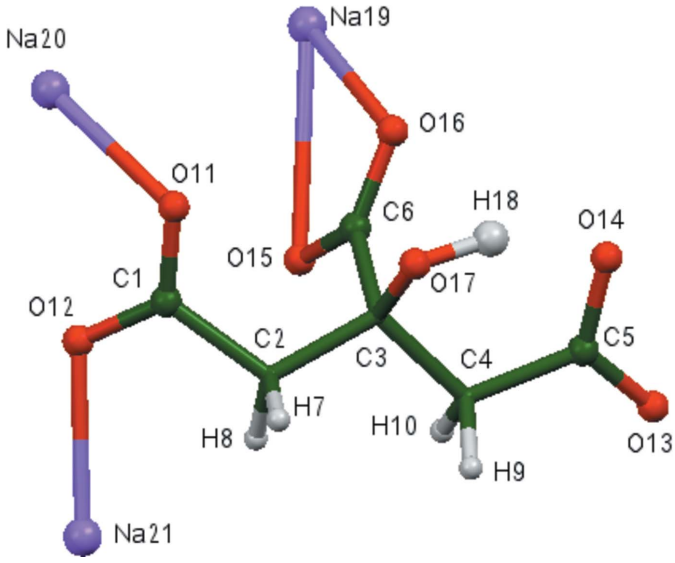


Figure 1
The asymmetric unit, showing the atom numbering. The atoms are represented by 50% probability spheroids.

2. Structural commentary

The asymmetric unit of the title compound is shown in Fig. 1. The root-mean-square deviation of the non-hydrogen atoms in the Rietveld refined and the optimized structure using density functional theory (DFT) is only 0.057 Å. The maximum deviation is 0.103 Å, at Na19. The excellent agreement between the two structures (Fig. 2) is strong evidence that the experimental structure is correct (van de Streek & Neumann, 2014). This discussion uses the DFT-optimized structure. All of the bond lengths, bond angles, and torsion angles fall within the normal ranges indicated by a *Mercury Mogul* geometry check (Macrae *et al.*, 2008). The hydroxyl group bridges atoms Na20 and Na21. The citrate anion 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. The central carboxylate group and the hydroxyl group occur in the normal planar arrangement. The central carboxylate group C6–O15–O16 chelates to Na19, and the terminal carboxylate C5–O13–O14 chelates to Na21. The citrate chelates to Na20 through the hydroxyl group O17 and the terminal carboxylate C1–O11–O12, and to a second Na19 through the terminal carboxylate oxygen atom O14 and the central carboxylate oxygen atom O16. Na19 is five-coordinate (irregular) with a bond-valence sum of 1.08. Na20 is six-coordinate (distorted octahedral) with a bond-valence sum of 1.14. Na21 is five-coordinate (trigonal–bipyramidal) with a bond-valence sum of 1.01. The metal–oxygen bonding is ionic, based on the cation charges and Mulliken overlap populations.

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

D—H···A	D—H	H···A	D···A	D—H···A
O17—H18···O14	0.987	1.805	2.671	144.0
C2—H8···O17^{i}	1.086	2.356	3.355	152.2

Symmetry code: (i) $x, y-1, z$.

3. Supramolecular features

There are two independent five-coordinate and one six-coordinate Na^{+} cations in the asymmetric unit. The [NaO_5] and [NaO_6] polyhedra share edges and corners to form a three-dimensional framework (Fig. 3). There are channels parallel to the *a* and *b* axes in which the remainder of the citrate anions reside. The only hydrogen bond is an intramolecular O17–H18···O14 one between the hydroxy group and one of the terminal carboxylate O atoms (Table 1). One intermolecular C—H···O hydrogen bond also apparently contributes to the crystal packing.

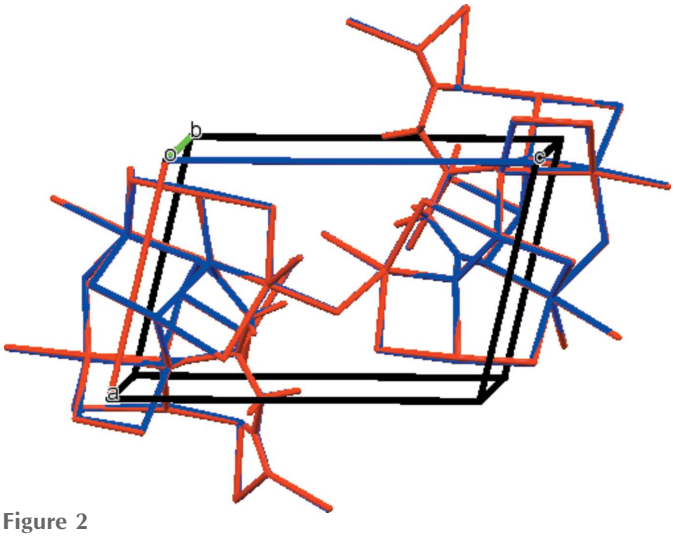


Figure 2
Comparison of the refined and optimized structures of trisodium citrate. The refined structure is in red, and the DFT-optimized structure is in blue.

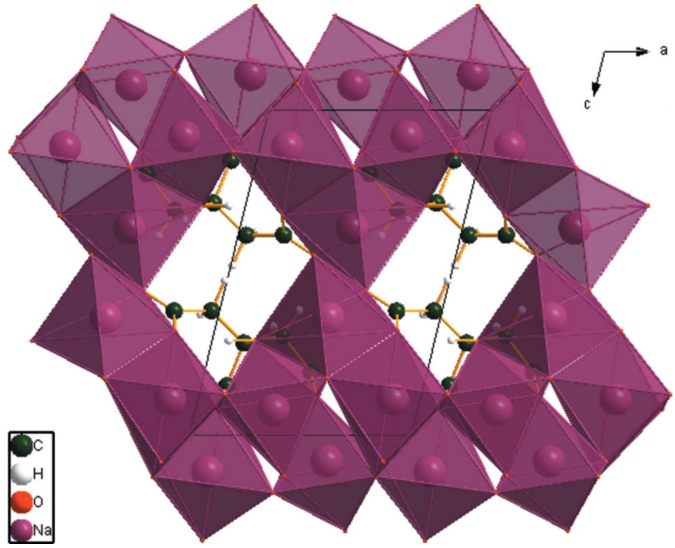


Figure 3
Crystal structure of $Na_3(C_6H_5O_7)$, viewed down the *b* axis.

Table 2
Experimental details.

	Phase_1	Phase_2
Crystal data		
Chemical formula	$Na_3(C_6H_5O_7)$	$C_6H_5O_7{\cdot}2H_2O$
M_r	258.07	98.03
Crystal system, space group	Monoclinic, $P2_1$	Monoclinic, $C2/c$
Temperature (K)	293	293
a, b, c (Å)	7.34705 (5), 5.43482 (4), 11.03447 (7)	15.7057 (5), 12.5045 (5), 11.2945 (8)
β (°)	103.8797 (6)	103.611 (4)
V (Å^3)	427.74 (1)	2155.84 (12)
Z	2	2
Radiation type	Synchrotron, λ = 0.41307 Å	Synchrotron, λ = 0.41307 Å
μ (mm^{-1})	0.02	0.02
Specimen shape, size (mm)	Cylinder, 1.5 × 1.5	Cylinder, 1.5 × 1.5
Data collection		
Diffractometer	11-BM APS	11-BM APS
Specimen mounting	Kapton capillary	Kapton capillary
Data collection mode	Transmission	Transmission
Scan method	Step	Step
2θ values (°)	$2\theta_{min}$ = 0.5 $2\theta_{max}$ = 50.0 $2\theta_{step}$ = 0.001	$2\theta_{min}$ = 0.5 $2\theta_{max}$ = 50.0 $2\theta_{step}$ = 0.001
Refinement		
R factors and goodness of fit	R_p = 0.059, R_{wp} = 0.073, R_{exp} = 0.062, $R(F^2)$ = 0.06382, χ^2 = 1.416	R_p = 0.059, R_{wp} = 0.073, R_{exp} = 0.062, $R(F^2)$ = 0.06382, χ^2 = 1.416
No. of parameters	73	73
No. of restraints	29	29

The same symmetry and lattice parameters were used for the DFT calculation. Computer programs: *DIFFRAC* (Bruker, 2009), *PowDLL* (Kourkoumelis, 2013), *GSAS* (Larson & Von Dreele, 2004), *EXPGUI* (Toby, 2001), *DIAMOND* (Brandenburg, 2006) and *publCIF* (Westrip, 2010).

4. Database survey

Details of the comprehensive literature search for citrate structures are presented in Rammohan & Kaduk (2016*a*). A reduced cell in the Cambridge Structural Database (Groom *et al.*, 2016) search (increasing the default tolerance from 1.5 to 2.0%) yielded 19 hits, but limiting the chemistry to C, H, Na, and O only resulted in no hits. The powder pattern matched no entry in the Powder Diffraction File (ICDD, 2015).

5. Synthesis and crystallization

The sample was purchased from Sigma–Aldrich (lot #119K0107V) as anhydrous $Na_3(C_6H_5O_7)$. A laboratory powder pattern confirmed its phase purity. In the one year between this measurement and the measurement of the synchrotron pattern, the sample had partially hydrated to contain $Na_3(C_6H_5O_7)(H_2O)_2$ (UMOGAE; Fischer & Palladino, 2003).

6. Refinement details

Both laboratory and synchrotron patterns could be indexed (*DICVOL06*; Louër & Boultif, 2007) on a primitive monoclinic cell having a = 7.34705 (5), b = 5.43481 (4), c = 11.03449 (7) Å, β = 103.8 (6)°, and V = 427.740 (5) Å^3. The systematic absences were consistent with space group $P2_1$ (No. 4). All attempts to solve the structure using direct methods, charge flipping, and Monte Carlo simulated annealing (using a citrate and 3 Na) failed using this unit cell. Using the synchrotron pattern was complicated by the presence of 12.8 (1) wt% $Na_3(C_6H_5O_7)(H_2O)_2$ (UMOGAE; Fischer & Palladino, 2003). Since the cell of the anhydrous compound is approximately $\frac{1}{2}a$, $\frac{1}{2}b$, c that of the $C2/c$ cell of UMOGAE, unsuccessful attempts to solve the structure were also made in

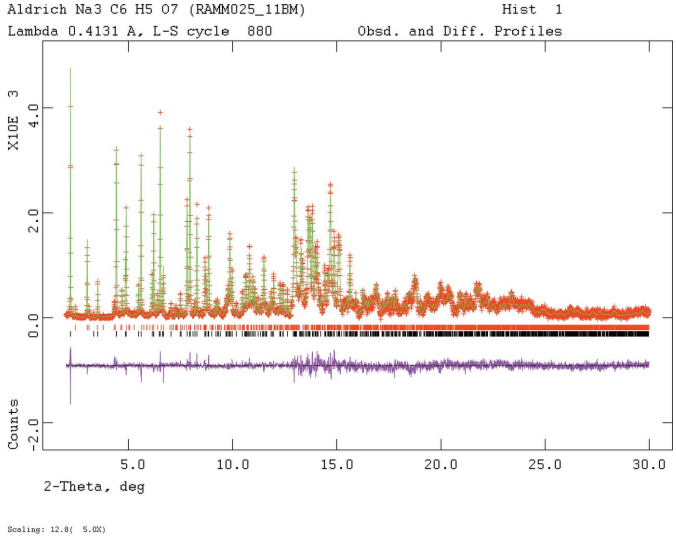


Figure 4
Rietveld plot for the refinement of $Na_3(C_6H_5O_7)$. The red crosses represent the observed data points, and the green line is the calculated pattern. The magenta curve is the difference pattern, plotted at the same scale as the other patterns. The vertical scale has been multiplied by a factor of 5 for $2\theta > 12.8°$. The lower row of black tick marks indicates the reflection positions for the major phase and the upper row of red tick marks is for the dihydrate impurity.

2× and 4× supercells of the observed cell. The powder pattern (Fig. 4) was indexed using *Jade 9.5* (MDI, 2012). Pseudo-Voigt profile coefficients were as parameterized in Thompson *et al.* (1987), and the asymmetry correction of Finger *et al.* (1994) was applied and microstrain broadening by Stephens (1999).

The structure was ultimately solved with *FOX* (Favre-Nicolin & Černý, 2002) using laboratory data from a single-phase dehydrated sample. A single $Na_3(C_6H_5O_7)$ fragment was derived from UMOGAE, with Na bound to the hydroxyl group, the central carboxyl group, and one of the terminal carboxyl groups. Attempts were made using both bump-check and bond-valence restraints, but the ultimate solution came without applying these restraints. This model refined reasonably well, but the bond-valence sums of the Na atom were unreasonable. A Hartree–Fock geometry optimization was carried out using *CRYSTAL09* (Dovesi *et al.*, 2005), and the resulting model (which had Na bond-valence sums 2) led to a successful refinement. All C—C and C—O bond lengths were restrained, as were all bond angles. The hydrogen atoms were included at fixed positions, which were re-calculated using *Materials Studio* (Dassault Systemes, 2014) during the course of the refinement. 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 × 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. Crystal data, data collection and structure refinement details are summarized in Table 2. The structure of the UMOGAE impurity was not refined.

The Bravais–Friedel–Donnay–Harker (Bravais, 1866; Friedel, 1907; Donnay & Harker, 1937) morphology suggests that we might expect platy morphology for trisodium citrate, with {001} as the principal faces. No texture model was necessary in the refinement, showing that preferred orientation was not significant for the rotated capillary specimen.

7. DFT calculations

After the Rietveld refinement, a density functional geometry optimization (fixed experimental unit cell) was carried out using *CRYSTAL09* (Dovesi *et al.*, 2005). The basis sets for the C, H, and O atoms were those of Gatti *et al.* (1994), and the basis set for Na was that of Dovesi *et al.* (1991). The calculation used 8 *k*-points and the B3LYP functional, and took about 42 h on a 2.8 GHz PC. The U_{iso} from the Rietveld refinement were assigned to the optimized fractional coordinates.

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Trisodium citrate, $Na_3(C_6H_5O_7)$

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Computing details

(Na3Citrate_phase_1) Trisodium citrate

Crystal data

$Na_3(C_6H_5O_7)$
M_r = 258.07
Monoclinic, $P2_1$
Hall symbol: P 2yb
a = 7.34705 (5) Å
b = 5.43482 (4) Å
c = 11.03447 (7) Å
β = 103.8797 (6)°
V = 427.74 (1) Å^3
Z = 2
T = 293 K

Data collection

$2\theta_{min}$ = 0.5°, $2\theta_{max}$ = 50.0°, $2\theta_{step}$ = 0.001°

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5224 (5)	0.38175	0.1958 (4)	0.0157 (4)*
C2	0.6922 (5)	0.3880 (11)	0.3074 (3)	0.0067 (9)*
C3	0.8567 (5)	0.5386 (10)	0.2868 (3)	0.0067 (9)*
C4	1.0366 (5)	0.4640 (10)	0.3842 (4)	0.0067 (9)*
C5	1.2023 (5)	0.6347 (10)	0.3794 (4)	0.0157 (4)*
C6	0.8848 (6)	0.4726 (10)	0.1548 (4)	0.0157 (4)*
H7	0.6428	0.46664	0.38548	0.0087 (11)*
H8	0.74029	0.20195	0.33589	0.0087 (11)*
H9	1.00831	0.48799	0.4767	0.0087 (11)*
H10	1.08026	0.28777	0.37225	0.0087 (11)*
O11	0.4714 (5)	0.5729 (8)	0.1317 (3)	0.0157 (4)*
O12	0.4413 (5)	0.1760 (8)	0.1782 (3)	0.0157 (4)*
O13	1.3623 (4)	0.5618 (9)	0.4457 (3)	0.0157 (4)*
O14	1.1800 (4)	0.8466 (10)	0.3267 (3)	0.0157 (4)*
O15	0.8895 (5)	0.2494 (9)	0.1281 (3)	0.0157 (4)*
O16	0.9014 (5)	0.6501 (10)	0.0875 (3)	0.0157 (4)*
O17	0.8078 (4)	0.7917 (8)	0.2931 (3)	0.0157 (4)*
H18	0.92601	0.87924	0.29256	0.0205 (5)*
Na19	−0.1355 (3)	−0.5364 (7)	−0.10917 (18)	0.0232 (4)*
Na20	−0.3462 (3)	−0.0710 (8)	0.07677 (18)	0.0232 (4)*
Na21	0.5075 (3)	−0.0927 (8)	0.35877 (15)	0.0232 (4)*

Geometric parameters (Å, º)

C1—C2	1.529 (3)	O13—Na21^{i}	2.465 (4)
C1—O11	1.262 (4)	O13—Na21^{iv}	2.299 (4)
C1—O12	1.260 (4)	O14—C5	1.282 (4)
C2—C1	1.529 (3)	O14—Na19^{v}	2.429 (3)
C2—C3	1.521 (3)	O14—Na21^{i}	2.370 (3)
C2—H7	1.098 (4)	O15—C6	1.251 (4)
C2—H8	1.092 (6)	O15—Na19^{vi}	2.430 (4)
C3—C2	1.521 (3)	O15—Na20^{iii}	2.425 (4)
C3—C4	1.544 (3)	O16—C6	1.241 (4)
C3—C6	1.560 (3)	O16—Na19^{i}	2.351 (3)
C3—O17	1.427 (4)	O16—Na19^{v}	2.392 (4)
C4—C3	1.544 (3)	O16—Na20^{i}	2.349 (4)
C4—C5	1.542 (3)	O17—C3	1.427 (4)
C4—H9	1.097 (4)	O17—H18	0.992 (3)
C4—H10	1.029 (5)	O17—Na20^{i}	2.497 (4)
C5—C4	1.542 (3)	O17—Na21^{vii}	2.561 (4)
C5—O13	1.289 (4)	H18—O17	0.992 (3)
C5—O14	1.282 (4)	Na19—O12^{viii}	2.478 (4)
C6—C3	1.560 (3)	Na19—O14^{ix}	2.429 (3)
C6—O15	1.251 (4)	Na19—O15^{x}	2.430 (4)
C6—O16	1.241 (4)	Na19—O16^{xi}	2.351 (3)
H7—C2	1.098 (4)	Na19—O16^{ix}	2.392 (4)
H8—C2	1.092 (6)	Na20—O11^{xi}	2.509 (4)
H9—C4	1.097 (4)	Na20—O11^{viii}	2.394 (4)
H10—C4	1.029 (5)	Na20—O12^{xii}	2.516 (4)
O11—C1	1.262 (4)	Na20—O15^{xii}	2.425 (4)
O11—Na20^{i}	2.509 (4)	Na20—O16^{xi}	2.349 (4)
O11—Na20^{ii}	2.394 (4)	Na20—O17^{xi}	2.497 (4)
O12—C1	1.260 (4)	Na21—O12	2.424 (4)
O12—Na19^{ii}	2.478 (4)	Na21—O13^{xi}	2.465 (4)
O12—Na20^{iii}	2.516 (4)	Na21—O13^{xiii}	2.299 (4)
O12—Na21	2.424 (4)	Na21—O14^{xi}	2.370 (3)
O13—C5	1.289 (4)	Na21—O17^{xiv}	2.561 (4)
C2—C1—O11	120.6 (4)	C6—O16—Na19^{i}	102.2 (3)
C2—C1—O12	114.1 (4)	C6—O16—Na19^{v}	131.7 (3)
O11—C1—O12	125.3 (4)	C6—O16—Na20^{i}	110.2 (3)
C1—C2—C3	114.5 (3)	Na19^{i}—O16—Na19^{v}	108.68 (13)
C1—C2—H7	106.3 (3)	Na19^{i}—O16—Na20^{i}	108.37 (18)
C1—C2—H8	110.9 (4)	Na19^{v}—O16—Na20^{i}	94.30 (16)
C3—C2—H7	109.4 (4)	C3—O17—H18	103.4 (3)
C3—C2—H8	109.1 (3)	C3—O17—Na20^{i}	107.7 (2)
H7—C2—H8	106.2 (3)	C3—O17—Na21^{vii}	119.6 (3)
C2—C3—C4	109.4 (3)	H18—O17—Na20^{i}	92.7 (2)
C2—C3—C6	107.7 (3)	H18—O17—Na21^{vii}	134.4 (3)
C2—C3—O17	107.0 (3)	Na20^{i}—O17—Na21^{vii}	88.49 (12)

C4—C3—C6	107.9 (3)	O12^{viii}—Na19—O14^{ix}	85.47 (12)
C4—C3—O17	113.8 (3)	O12^{viii}—Na19—O15^{x}	108.30 (14)
C6—C3—O17	111.0 (3)	O12^{viii}—Na19—O16^{xi}	88.75 (14)
C3—C4—C5	111.7 (3)	O12^{viii}—Na19—O16^{ix}	160.03 (14)
C3—C4—H9	107.2 (3)	O14^{ix}—Na19—O15^{x}	90.50 (12)
C3—C4—H10	113.4 (4)	O14^{ix}—Na19—O16^{xi}	169.63 (18)
C5—C4—H9	106.7 (4)	O14^{ix}—Na19—O16^{ix}	80.52 (13)
C5—C4—H10	106.4 (4)	O15^{x}—Na19—O16^{xi}	83.13 (14)
H9—C4—H10	111.4 (4)	O15^{x}—Na19—O16^{ix}	86.11 (13)
C4—C5—O13	114.6 (4)	O16^{xi}—Na19—O16^{ix}	107.09 (11)
C4—C5—O14	122.7 (4)	O11^{xi}—Na20—O11^{viii}	112.30 (11)
O13—C5—O14	122.2 (4)	O11^{xi}—Na20—O12^{xii}	83.09 (12)
C3—C6—O15	117.4 (4)	O11^{xi}—Na20—O15^{xii}	152.88 (15)
C3—C6—O16	115.7 (3)	O11^{xi}—Na20—O16^{xi}	86.68 (13)
O15—C6—O16	126.9 (4)	O11^{xi}—Na20—O17^{xi}	71.61 (12)
C2—H7—Na21^{vii}	117.5 (3)	O11^{viii}—Na20—O12^{xii}	96.69 (13)
C2—H8—Na21	117.30 (18)	O11^{viii}—Na20—O15^{xii}	94.48 (13)
C1—O11—Na20^{i}	131.8 (3)	O11^{viii}—Na20—O16^{xi}	111.95 (14)
C1—O11—Na20^{ii}	105.3 (3)	O11^{viii}—Na20—O17^{xi}	175.68 (13)
Na20^{i}—O11—Na20^{ii}	97.15 (12)	O12^{xii}—Na20—O15^{xii}	89.86 (13)
C1—O12—Na19^{ii}	145.2 (3)	O12^{xii}—Na20—O16^{xi}	151.35 (15)
C1—O12—Na20^{iii}	102.8 (3)	O12^{xii}—Na20—O17^{xi}	85.50 (13)
C1—O12—Na21	114.5 (3)	O15^{xii}—Na20—O16^{xi}	87.17 (12)
Na19^{ii}—O12—Na20^{iii}	103.21 (13)	O15^{xii}—Na20—O17^{xi}	81.78 (12)
Na19^{ii}—O12—Na21	87.73 (12)	O16^{xi}—Na20—O17^{xi}	65.87 (12)
Na20^{iii}—O12—Na21	91.19 (13)	O12—Na21—O13^{xi}	139.35 (12)
C5—O13—Na21^{i}	88.0 (3)	O12—Na21—O13^{xiii}	120.53 (15)
C5—O13—Na21^{iv}	139.7 (3)	O12—Na21—O14^{xi}	88.00 (12)
Na21^{i}—O13—Na21^{iv}	121.45 (13)	O12—Na21—O17^{xiv}	86.08 (13)
C5—O14—Na19^{v}	130.9 (4)	O13^{xi}—Na21—O13^{xiii}	91.98 (9)
C5—O14—Na21^{i}	92.4 (2)	O13^{xi}—Na21—O14^{xi}	55.47 (10)
Na19^{v}—O14—Na21^{i}	90.11 (11)	O13^{xi}—Na21—O17^{xiv}	113.94 (16)
C6—O15—Na19^{vi}	134.7 (4)	O13^{xiii}—Na21—O14^{xi}	111.71 (13)
C6—O15—Na20^{iii}	133.8 (4)	O13^{xiii}—Na21—O17^{xiv}	99.35 (12)
Na19^{vi}—O15—Na20^{iii}	91.44 (12)	O14^{xi}—Na21—O17^{xiv}	146.79 (15)

Symmetry codes: (i) $x+1, y+1, z$; (ii) $-x, y+1/2, -z$; (iii) $x+1, y, z$; (iv) $-x+2, y+1/2, -z+1$; (v) $-x+1, y+3/2, -z$; (vi) $-x+1, y+1/2, -z$; (vii) $x, y+1, z$; (viii) $-x, y-1/2, -z$; (ix) $-x+1, y-3/2, -z$; (x) $-x+1, y-1/2, -z$; (xi) $x-1, y-1, z$; (xii) $x-1, y, z$; (xiii) $-x+2, y-1/2, -z+1$; (xiv) $x, y-1, z$.

(Na3Citrate_phase_2)

Crystal data

$C_6H_5O_7(H2O)_2$
$M_r = 98.03$
Monoclinic, $C2/c$
$a = 15.7057$ (5) Å
$b = 12.5045$ (5) Å
$c = 11.2945$ (8) Å
$\beta = 103.611$ (4)°
$V = 2155.84$ (12) Å^3
$Z = 2$
$T = 293$ K

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.32032	0.26746	−0.12039	0.025*
C2	0.40138	0.20513	−0.13157	0.025*
H1	0.3843	0.132	−0.1542	0.025*
H2	0.4238	0.236	−0.1971	0.025*
C3	0.47454	0.20354	−0.01659	0.025*
C4	0.54966	0.13205	−0.03589	0.025*
H3	0.5241	0.0686	−0.0795	0.025*
H4	0.5802	0.1701	−0.0884	0.025*
C5	0.61747	0.09605	0.0773	0.025*
C6	0.5119	0.31612	0.01854	0.025*
Na1	0.39983	0.49615	−0.10199	0.025*
Na2	0.38687	0.32751	0.17398	0.025*
Na3	0.31278	0.07827	0.12757	0.025*
O1	0.3292	0.34512	−0.04739	0.025*
O2	0.24806	0.23955	−0.18727	0.025*
O3	0.69001	0.06577	0.06113	0.025*
O4	0.59581	0.09256	0.17743	0.025*
O5	0.52668	0.37453	−0.06565	0.025*
O6	0.52678	0.34375	0.12801	0.025*
O7	0.43809	0.16051	0.07907	0.025*
H5	0.4811	0.1391	0.13	0.025*
O8	0.35892	0.51957	0.1855	0.025*
H6	0.3903	0.5577	0.157	0.025*
H7	0.3062	0.534	0.153	0.025*
O9	0.23658	−0.0877	0.13185	0.025*
H8	0.2578	−0.105	0.0759	0.025*
H9	0.2422	−0.1312	0.1864	0.025*

Geometric parameters (Å, º)

C1—C2	1.5231 (1)	Na3—O2^{iii}	2.6193 (1)
C1—O1	1.2602 (1)	Na3—O3^{v}	2.7829 (1)
C1—O2	1.2557 (1)	Na3—O4^{iv}	2.3357 (2)
C2—C1	1.5231 (1)	Na3—O7	2.3955 (1)
C2—H1	0.9702 (1)	Na3—O9	2.4019 (1)
C2—H2	0.9713 (1)	O1—C1	1.2602 (1)
C2—C3	1.5182 (1)	O1—Na1	2.3451 (1)
H1—C2	0.9702 (1)	O1—Na2	2.4606 (2)
H1—H2	1.5660 (1)	O1—Na3^{iii}	2.4000 (1)
H2—C2	0.9713 (1)	O2—C1	1.2557 (1)
H2—H1	1.5660 (1)	O2—Na2^{iii}	2.3165 (1)
C3—C2	1.5182 (1)	O2—Na3^{iii}	2.6193 (1)
C3—C4	1.5361 (1)	O3—C5	1.2541 (1)
C3—C6	1.5408 (1)	O3—Na3^{v}	2.7829 (1)
C3—O7	1.4407 (1)	O4—C5	1.2561 (1)

C4—C3	1.5361 (1)	O4—Na3^{iv}	2.3357 (2)
C4—H3	0.9696 (1)	O5—C6	1.2631 (1)
C4—H4	0.9706 (1)	O5—Na1	2.4628 (1)
C4—C5	1.5266 (1)	O5—Na1^{i}	2.5502 (1)
H3—C4	0.9696 (1)	O6—C6	1.2517 (1)
H3—H4	1.5617 (1)	O6—Na1^{i}	2.3627 (1)
H4—C4	0.9706 (1)	O6—Na2	2.3825 (1)
H4—H3	1.5617 (1)	O6—Na2^{iv}	2.3355 (2)
C5—C4	1.5266 (1)	O7—C3	1.4407 (1)
C5—O3	1.2541 (1)	O7—Na2	2.5618 (1)
C5—O4	1.2561 (1)	O7—Na3	2.3955 (1)
C6—C3	1.5408 (1)	O7—H5	0.8222 (1)
C6—O5	1.2631 (1)	H5—O7	0.8222 (1)
C6—O6	1.2517 (1)	O8—Na1^{vi}	2.3423 (2)
Na1—O1	2.3451 (1)	O8—Na2	2.4504 (1)
Na1—O5	2.4628 (1)	O8—H6	0.8053 (1)
Na1—O5^{i}	2.5502 (1)	O8—H7	0.8425 (1)
Na1—O6^{i}	2.3627 (1)	H6—O8	0.8053 (1)
Na1—O8^{ii}	2.3423 (2)	H7—O8	0.8425 (1)
Na1—O9^{iii}	2.3821 (1)	O9—Na1^{iii}	2.3821 (1)
Na2—O1	2.4606 (2)	O9—Na3	2.4019 (1)
Na2—O2^{iii}	2.3165 (1)	O9—H8	0.8101 (1)
Na2—O6	2.3825 (1)	O9—H9	0.8110 (1)
Na2—O6^{iv}	2.3355 (2)	H8—O9	0.8101 (1)
Na2—O7	2.5618 (1)	H8—H9	1.3671 (1)
Na2—O8	2.4504 (1)	H9—O9	0.8110 (1)
Na3—O1^{iii}	2.4000 (1)		

C2—C1—O1	118.855 (3)	O1^{vii}—Na3—O3^{v}	97.099 (4)
C2—C1—O2	117.557 (3)	O1^{vii}—Na3—O4^{iv}	129.465 (3)
O1—C1—O2	123.567 (2)	O1^{vii}—Na3—O7	118.866 (3)
C1—C2—H1	108.632 (2)	O1^{vii}—Na3—O9	85.950 (3)
C1—C2—H2	108.650 (3)	O1^{vii}—Na3—H8	92.239 (3)
C1—C2—C3	114.514 (3)	O2^{vii}—Na3—O3^{v}	144.9968 (19)
H1—C2—H2	107.529 (3)	O2^{vii}—Na3—O4^{iv}	82.602 (2)
H1—C2—C3	108.6447 (14)	O2^{vii}—Na3—O7	93.131 (3)
H2—C2—C3	108.656 (4)	O2^{vii}—Na3—O9	122.184 (3)
C2—C3—C4	109.767 (3)	O2^{vii}—Na3—H8	137.676 (2)
C2—C3—C6	111.9638 (16)	O3^{v}—Na3—O4^{iv}	131.841 (3)
C2—C3—O7	106.981 (4)	O3^{v}—Na3—O7	88.191 (4)
C4—C3—C6	108.035 (3)	O3^{v}—Na3—O9	62.487 (3)
C4—C3—O7	110.065 (3)	O3^{v}—Na3—H8	43.6914 (19)
C6—C3—O7	110.033 (3)	O4^{iv}—Na3—O7	80.039 (4)
C3—C4—H3	107.956 (3)	O4^{iv}—Na3—O9	104.225 (2)
C3—C4—H4	107.935 (3)	O4^{iv}—Na3—H8	113.3843 (12)
C3—C4—C5	117.421 (3)	O7—Na3—O9	144.6477 (4)
H3—C4—H4	107.204 (4)	O7—Na3—H8	127.2020 (15)
H3—C4—C5	107.936 (3)	O9—Na3—H8	19.0777 (12)

H4—C4—C5	107.973 (3)	C1—O1—Na1	115.778 (4)
C4—C5—O3	116.471 (4)	C1—O1—Na2	123.604 (3)
C4—C5—O4	118.742 (4)	C1—O1—Na3^{vii}	96.360 (4)
O3—C5—O4	124.644 (4)	Na1—O1—Na2	104.803 (3)
C3—C6—Na1^{i}	171.7217 (3)	Na1—O1—Na3^{vii}	91.967 (2)
C3—C6—O5	117.438 (3)	Na2—O1—Na3^{vii}	120.418 (4)
C3—C6—O6	118.5445 (15)	C1—O2—Na2^{vii}	140.595 (3)
O5—C6—O6	124.011 (3)	C1—O2—Na3^{vii}	86.344 (2)
O1—Na1—O5	82.707 (3)	Na2^{vii}—O2—Na3^{vii}	84.459 (2)
O1—Na1—O5^{i}	118.350 (4)	C5—O3—Na3^{v}	117.119 (3)
O1—Na1—O6^{i}	171.8454 (5)	C5—O4—Na3^{iv}	127.955 (4)
O1—Na1—O8^{vi}	99.742 (3)	C6—O5—Na1	101.406 (3)
O1—Na1—O9^{vii}	87.646 (3)	C6—O5—Na1^{i}	86.502 (4)
O5—Na1—O5^{i}	93.485 (4)	Na1—O5—Na1^{i}	86.515 (4)
O5—Na1—O6^{i}	98.324 (3)	C6—O6—Na1^{i}	95.403 (3)
O5—Na1—O8^{vi}	97.759 (4)	C6—O6—Na2	102.965 (4)
O5—Na1—O9^{vii}	170.2946 (2)	C6—O6—Na2^{iv}	148.568 (2)
O5^{i}—Na1—O6^{i}	53.577 (3)	Na1^{i}—O6—Na2	126.9628 (11)
O5^{i}—Na1—O8^{vi}	141.360 (2)	Na1^{i}—O6—Na2^{iv}	90.140 (2)
O5^{i}—Na1—O9^{vii}	92.018 (4)	Na2—O6—Na2^{iv}	98.130 (4)
O6^{i}—Na1—O8^{vi}	88.158 (3)	C3—O7—Na2	103.220 (3)
O6^{i}—Na1—O9^{vii}	91.377 (3)	C3—O7—Na3	145.553 (3)
O8^{vi}—Na1—O9^{vii}	82.794 (4)	C3—O7—H5	103.901 (4)
O1—Na2—O2^{vii}	88.547 (4)	Na2—O7—Na3	84.172 (3)
O1—Na2—O6	84.765 (4)	Na2—O7—H5	105.063 (3)
O1—Na2—O6^{iv}	163.1753 (13)	Na3—O7—H5	106.510 (3)
O1—Na2—O7	74.009 (3)	Na1^{viii}—O8—Na2	87.8676 (11)
O1—Na2—O8	86.4762 (11)	Na1^{viii}—O8—H6	114.405 (3)
O2^{vii}—Na2—O6	161.7469 (8)	Na1^{viii}—O8—H7	117.962 (4)
O2^{vii}—Na2—O6^{iv}	107.659 (4)	Na2—O8—H6	115.146 (2)
O2^{vii}—Na2—O7	96.556 (3)	Na2—O8—H7	110.9005 (7)
O2^{vii}—Na2—O8	99.9795 (16)	H6—O8—H7	109.281 (3)
O6—Na2—O6^{iv}	81.011 (4)	Na1^{vii}—O9—Na3	91.014 (3)
O6—Na2—O7	65.276 (2)	Na1^{vii}—O9—H8	122.635 (4)
O6—Na2—O8	96.5444 (9)	Na1^{vii}—O9—H9	111.307 (3)
O6^{iv}—Na2—O7	107.626 (2)	Na3—O9—H8	85.218 (2)
O6^{iv}—Na2—O8	86.2643 (9)	Na3—O9—H9	128.990 (3)
O7—Na2—O8	154.0227 (14)	H8—O9—H9	114.980 (4)
O1^{vii}—Na3—O2^{vii}	52.202 (2)		

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*; (ii) *x*, −*y*+1, *z*−1/2; (iii) −*x*−1/2, −*y*−1/2, −*z*; (iv) −*x*+1, *y*, −*z*+1/2; (v) −*x*+1, −*y*, −*z*; (vi) *x*, −*y*+1, *z*+1/2; (vii) −*x*+1/2, −*y*+1/2, −*z*; (viii) *x*, −*y*+1, *z*+3/2.

(Na3Citrate_DFT)

Crystal data

$Na_3C_6H_5O_7$	*a* = 7.3471 Å
M_r = 258.07	*b* = 5.4348 Å
Monoclinic, $P2_1$	*c* = 11.0345 Å

β = 103.8797°
V = 427.72 Å^3
Z = 2

None radiation, λ = 1.5418 Å
T = 300 K

Data collection

Density functional calculation
$h = \rightarrow$

$k = \rightarrow$
$l = \rightarrow$

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.52139	0.36379	0.19408	0.01570*
C2	0.68978	0.38591	0.30743	0.00670*
C3	0.85441	0.53721	0.28438	0.00670*
C4	1.03620	0.47678	0.38367	0.00670*
C5	1.20386	0.64379	0.38297	0.01570*
C6	0.88406	0.47193	0.15320	0.01570*
H7	0.64280	0.46663	0.38548	0.00870*
H8	0.74029	0.20195	0.33589	0.00870*
H9	1.00831	0.48799	0.47670	0.00870*
H10	1.08026	0.28777	0.37225	0.00870*
O11	0.47255	0.54929	0.12466	0.01570*
O12	0.44290	0.15314	0.17676	0.01570*
O13	1.36310	0.57603	0.44517	0.01570*
O14	1.17738	0.84623	0.32240	0.01570*
O15	0.88375	0.24614	0.12627	0.01570*
O16	0.90355	0.64680	0.08168	0.01570*
O17	0.80788	0.79240	0.29212	0.01570*
H18	0.92601	0.87924	0.29256	0.02050*
Na19	−0.12326	0.46644	−0.11139	0.02321*
Na20	−0.35267	−0.09861	0.07904	0.02321*
Na21	0.50371	−0.08736	0.36215	0.02321*

Bond lengths (Å)

C1—C2	1.539	C4—C5	1.532
C1—O11	1.265	C4—H9	1.096
C1—O12	1.276	C4—H10	1.093
C2—C3	1.533	C5—O13	1.261
C2—H7	1.094	C5—O14	1.278
C2—H8	1.086	C6—O15	1.262
C3—C4	1.546	C6—O16	1.265
C3—C6	1.556	O17—H18	0.987
C3—O17	1.436		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O17—H18···O14	0.987	1.805	2.671	144.0

C2—H8···O17^{i}	1.086	2.356	3.355	152.2

Symmetry code: (i) x, $y-1$, z.