Sodium 1-carboxycyclopropane-1-carboxylate cyclopropane-1,1-di-carboxylic acid monohydrate

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In the title type B_2 acid salt, $Na(LH)(LH_2) \cdot H_2O$ [$LH_2 = C_2H_4C(CO_2H)_2$] or $Na^+ \cdot C_5H_5O_4^- \cdot C_5H_6O_4 \cdot H_2O$, the vertices of a distorted octahedron centred on each Na^+ cation are defined by six O atoms, one from a water molecule, one from an internally hydrogen-bonded LH^- anion and four from three neutral LH_2 acid molecules. Chains of edge-sharing O_6 octahedra are stabilized by hydrogen bonds, which interconnect the donor H_2O and LH_2 molecules and LH^- anions. In particular, the LH_2 molecule donates H atoms to LH^- and H_2O and forgoes the internal hydrogen bond which stabilizes the free acid and all of its characterized salts.

Comment

The cyclopropane-1,1-dicarboxylic acid molecule, (1), hereinafter LH_2, where L is $C_2H_4C(CO_2)_2$, contains an internal O—H···O hydrogen bond (see scheme) and, in consequence, its monoanion LH^-, (2), is a very weak acid (Meester *et al.*, 1971). The LH^- anions of the related acid salt $K(LH) \cdot 0.5H_2O$ are also stabilized by internal O—H···O hydrogen bonds (Dubourg *et al.*, 1990). We now report that our attempt to prepare the analogous sodium salt $Na(LH) \cdot 0.5H_2O$ has instead produced the title compound, $Na(LH)(LH_2) \cdot H_2O$, (I).
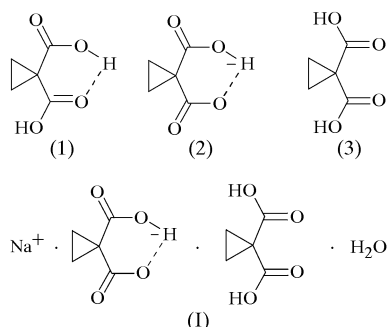
Crystals of (I) are built up from Na^+ cations, LH^- anions, molecules of the neutral acid and water. The LH^- anions
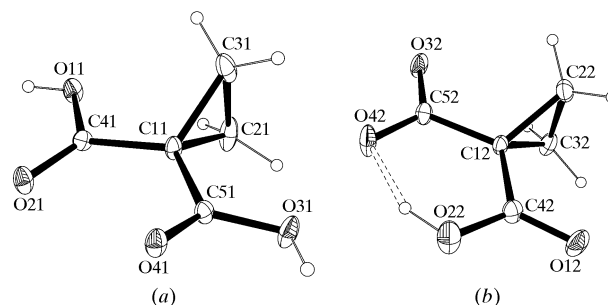

Figure 1
Views of (*a*) the LH_2 molecule and (*b*) the LH^- anion of (I). Displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as small spheres of arbitrary radii.

(Fig. 1*b*) contain an internal O—H···O hydrogen bond with an O···O distance of 2.429 (3) Å, which is even shorter than the corresponding bond in the free acid (2.563 Å). The internal O—H···O hydrogen bonds in the LH_2 molecule (Meester *et al.*, 1971) and in the LH^- anions of (I) and $K(LH) \cdot 0.5H_2O$ (Dubourg *et al.*, 1990) all have ordered H atoms conventionally bonded to one of the O atoms. This contrasts with $[Co(H_2O)_6](LH)_2$, where the anions straddle crystallographic mirror planes so that the acidic H atom is either equidistant from the two O atoms or is disordered (Schwarz *et al.*, 1998).

The LH_2 molecules of (I) (Fig. 1*a*) have near C_{2v} symmetry but adopt a conformation, (3), which precludes internal hydrogen bonding [O21···O41 = 2.834 (3) Å]. The geometries of the LH_2 molecule and LH^- anion (Table 1) show typical features (see, for example, Meester *et al.*, 1971; Dubourg *et al.*, 1990; Muir *et al.*, 2000; Schwarz *et al.*, 1998). First, pairs of C—O bond lengths differ by > 0.08 Å in CO_2H groups and by < 0.02 (5) Å in CO_2^- groups. Secondly, an electronic effect of the carboxyl substituents shortens the distal C2n—C3n ($n = 1$ or 2) ring bonds by 0.05–0.07 Å relative to the other C—C bonds in the cyclopropane rings. Finally, each carboxyl group nearly coincides with the plane normal to C2n—C3n passing through C1n; the C51 carboxyl group is an exception, as can be seen by comparing the C41—C11—C51—O41 torsion angle with the others in Table 1.

The crystal structure of (I) is built from kinked chains of identical NaO_6 octahedra (Table 1 and Fig. 2*a*), which are axially elongated along the O21···Na1···O1W direction and linked *via* edges which pass through crystallographic inversion centres. Atom Na1 shares octahedral edges with atoms Na1[i] and Na1[iii], themselves related directly by translation along the *a* axis which thus defines the direction of the chains [symmetry codes: (i) $1 - x$, $1 - y$, $2 - z$; (iii) $-x$, $1 - y$, $2 - z$].

Atom Na1 bonds to three different LH_2 molecules, one water molecule and one LH^- anion. In consequence, the LH_2 molecule participates in four Na—O bonds (Fig. 2*b*), with atom O2[i] bonded to both atoms Na1 and Na1[i], and atom O41[i] shared between atoms Na1 and Na[iii]. The LH^- anion is attached to only one cation, through atom O42, which is part of the ionized carboxyl group. Similarly, the water atom O1W

bonds to only one Na$^+$ cation. Each acid molecule is also the donor in two O—H···O hydrogen bonds (Table 2), namely a very strong bond [O···O = 2.478 (3) Å] to the LH^- anion and a weaker one [O···O = 2.642 (3) Å] to a water molecule. Atom O22 accepts a hydrogen bond from atom O1W. The resulting arrangement surrounds atoms Na1 and Na1^{iii} by a roughly planar belt containing an $(LH_2–LH^-–H_2O)_2$ ring in which the individual molecules and anions are joined by hydrogen bonds. Not shown in Fig. 2(b) are the O1W—H···O12 hydrogen bonds which link together the chains of octahedra.

The crystal architecture of (I) uses all five available O—H groups as hydrogen-bond donors, two of these bonds being very short (O···O < 2.50 Å). In each independent O—H···O bond, the two O atoms are unrelated by crystallographic symmetry. Compound (I) is therefore a B_2 acid salt in the classification of Speakman (1972).

It is tempting to ascribe the different stoichiometries of the sodium and potassium acid salts of cyclopropane-1,1-di-carboxylic acid to the different ionic radii of K$^+$ and 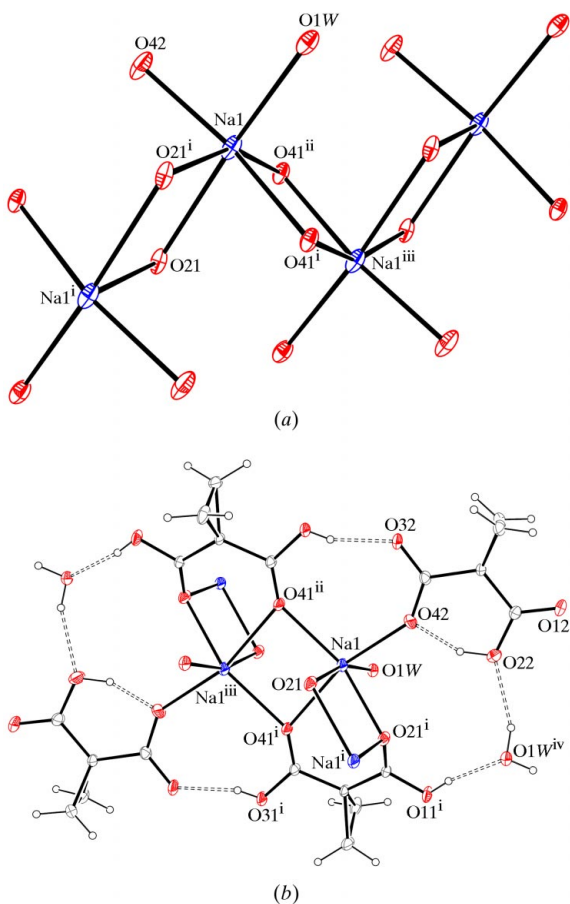Na$^+$. However, in the case of malonic acid, $L'H_2$, where L' is $CH_2(CO_2)_2$, a similar difference is the result of a solvent isotope effect: the salts Na(L'H) and Na(L'H)(LH_2) can be produced by identical procedures, but using D$_2$O as the solvent gives partially deuterated Na(L'H)(L'H$_2$), whereas H$_2$O gives Na(L'H) (Kalsbeek, 1992).

Experimental

Crystals of (I) were obtained from an aqueous solution containing sodium hydroxide and cyclopropane-1,1-dicarboxylic acid in a 1:2 molar ratio. The IR spectrum contains broad bands at 2480 and 1905 cm^{-1} attributable to unsymmetrical O—H···O hydrogen bonds.

Crystal data

Na$^+$·C$_5$H$_5$O$_4$$^-$·C$_5H_6O_4$·H$_2$O	$Z = 2$
$M_r = 300.19$	$D_x = 1.593$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 5.2910$ (13) Å	Cell parameters from 22
$b = 10.118$ (3) Å	reflections
$c = 12.895$ (5) Å	$\theta = 18.8–20.7°$
$\alpha = 109.44$ (3)°	$\mu = 0.17$ mm^{-1}
$\beta = 98.64$ (2)°	$T = 293$ (2) K
$\gamma = 99.57$ (2)°	Needle, white
$V = 626.0$ (4) Å^3	$0.48 \times 0.22 \times 0.16$ mm

Data collection

Enraf–Nonius CAD-4	$\theta_{max} = 28.0°$
diffractometer	$h = -6 \rightarrow 1$
Non-profiled ω scans	$k = -13 \rightarrow 13$
3932 measured reflections	$l = -17 \rightarrow 17$
2985 independent reflections	3 standard reflections
1654 reflections with $I > 2\sigma(I)$	frequency: 120 min
$R_{int} = 0.047$	intensity decay: 1%

Figure 2
(a) Part of the infinite chain of linked NaO$_6$ octahedra. (b) The hydrogen-bonded $(LH_2–LH^-–H_2O)_2$ belt around atoms Na1 and Na1^{iii}. Displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $1 - x$, $1 - y$, $2 - z$; (ii) $x - 1$, y, z; (iii) $-x$, $1 - y$, $2 - z$; (iv) $1 + x$, y, z.]

Table 1
Selected geometric parameters (Å, °).

Na1—O42	2.261 (2)	O41—C51	1.207 (3)
Na1—O21^i	2.325 (2)	C11—C21	1.513 (4)
Na1—O41^i	2.370 (2)	C11—C31	1.525 (4)
Na1—O41^{ii}	2.384 (2)	C21—C31	1.464 (5)
Na1—O1W	2.526 (3)	O12—C42	1.215 (3)
Na1—O21	2.533 (2)	O22—C42	1.298 (4)
Na1—Na1^{iii}	3.245 (2)	O32—C52	1.233 (3)
Na1—Na1^i	3.769 (3)	O42—C52	1.258 (4)
O11—C41	1.320 (3)	C12—C32	1.518 (4)
O21—C41	1.204 (3)	C12—C22	1.520 (4)
O31—C51	1.301 (3)	C22—C32	1.451 (5)
C51—C11—C41—O21	−1.4 (4)	C52—C12—C42—O22	−3.1 (4)
C41—C11—C51—O41	−23.0 (4)	C42—C12—C52—O42	1.9 (4)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O22—H22···O42	0.93 (6)	1.56 (6)	2.429 (3)	154 (5)
O1W—H2W···O12^v	0.86 (4)	1.90 (4)	2.737 (3)	162 (4)
O1W—H1W···O22^{ii}	0.85 (4)	1.98 (4)	2.777 (4)	155 (3)
O11—H11···O1W^{iii}	0.77 (5)	1.88 (5)	2.642 (3)	170 (5)
O31—H31···O32^{iv}	0.72 (6)	1.80 (6)	2.478 (3)	155 (6)

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

Refinement

Refinement on F^2	H atoms treated by a mixture of
$R(F) = 0.051$	independent and constrained
$wR(F^2) = 0.150$	refinement
$S = 0.99$	$w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$
2985 reflections	where $P = (F_o^2 + 2F_c^2)/3$
202 parameters	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.31$ e Å^{-3}
	$\Delta\rho_{min} = -0.36$ e Å^{-3}

H atoms were initially located in difference maps. In the final refinement, the positions of the methylene H atoms were determined by the HFIX instruction in *SHELXL*97 (Sheldrick, 1997) and they were then treated as riding on their parent C atoms, with C—H = 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C). The positional and isotropic displacement parameters of H atoms attached to O atoms were freely refined.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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supporting information

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Computing details

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1998).

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Crystal data

$Na^+ \cdot C_5H_5O_4^- \cdot C_5H_4O_4 \cdot H_2O$	$Z = 2$
$M_r = 300.19$	$F(000) = 312$
Triclinic, $P\bar{1}$	$D_x = 1.593$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 5.2910$ (13) Å	Cell parameters from 22 reflections
$b = 10.118$ (3) Å	$\theta = 18.8–20.7°$
$c = 12.895$ (5) Å	$\mu = 0.17$ mm^{-1}
$\alpha = 109.44$ (3)°	$T = 293$ K
$\beta = 98.64$ (2)°	Needle, white
$\gamma = 99.57$ (2)°	$0.48 \times 0.22 \times 0.16$ mm
$V = 626.0$ (4) Å^3	

Data collection

Enraf-Nonius CAD-4 diffractometer	$\theta_{max} = 28.0°$, $\theta_{min} = 4.7°$
non–profiled ω scans	$h = -6 \rightarrow 1$
3932 measured reflections	$k = -13 \rightarrow 13$
2985 independent reflections	$l = -17 \rightarrow 17$
1654 reflections with $I > 2\sigma(I)$	3 standard reflections every 120 min
$R_{int} = 0.047$	intensity decay: 1%

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.051$	$w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$
$wR(F^2) = 0.150$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.99$	$(\Delta/\sigma)_{max} < 0.001$
2985 reflections	$\Delta\rho_{max} = 0.31$ e Å^{-3}
202 parameters	$\Delta\rho_{min} = -0.36$ e Å^{-3}
0 restraints	

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Na1	0.1701 (2)	0.37779 (12)	0.97765 (9)	0.0352 (3)
O11	0.1927 (4)	0.5960 (2)	0.76510 (18)	0.0356 (5)
O21	0.4078 (4)	0.5633 (2)	0.91192 (15)	0.0336 (5)
O31	0.7072 (5)	0.2632 (2)	0.68504 (18)	0.0416 (6)
O41	0.8106 (4)	0.4147 (2)	0.86355 (15)	0.0301 (5)
C11	0.4859 (5)	0.4464 (3)	0.7284 (2)	0.0252 (6)
C21	0.3162 (7)	0.3705 (4)	0.6105 (2)	0.0469 (9)
H21A	0.3326	0.2744	0.5681	0.056*
H21B	0.14	0.3859	0.5973	0.056*
C31	0.5363 (7)	0.4912 (4)	0.6301 (2)	0.0449 (9)
H31A	0.4955	0.5809	0.6293	0.054*
H31B	0.6882	0.4692	0.6	0.054*
C41	0.3651 (5)	0.5410 (3)	0.8125 (2)	0.0237 (6)
C51	0.6834 (5)	0.3729 (3)	0.7681 (2)	0.0248 (6)
H11	0.148 (10)	0.650 (5)	0.813 (4)	0.086 (16)*
H31	0.791 (11)	0.222 (6)	0.703 (4)	0.11 (2)*
O12	0.6526 (4)	−0.1338 (2)	0.78279 (19)	0.0480 (6)
O22	0.6093 (5)	0.0705 (3)	0.9017 (2)	0.0597 (8)
O32	0.0016 (4)	0.0965 (2)	0.68459 (17)	0.0434 (6)
O42	0.2679 (4)	0.1867 (2)	0.85276 (18)	0.0494 (6)
C12	0.3214 (5)	−0.0282 (3)	0.7212 (2)	0.0261 (6)
C22	0.3379 (6)	−0.0868 (4)	0.5981 (2)	0.0412 (8)
H22A	0.2673	−0.0401	0.5495	0.049*
H22B	0.4927	−0.1215	0.5811	0.049*
C32	0.1525 (6)	−0.1714 (3)	0.6373 (2)	0.0387 (8)
H32A	0.1924	−0.2586	0.6444	0.046*
H32B	−0.0329	−0.1772	0.6129	0.046*
C42	0.5417 (6)	−0.0353 (3)	0.8047 (2)	0.0330 (6)
C52	0.1839 (5)	0.0932 (3)	0.7549 (2)	0.0303 (6)
H22	0.494 (12)	0.131 (6)	0.905 (5)	0.13 (2)*
O1W	0.0154 (5)	0.2282 (2)	1.0885 (2)	0.0379 (5)
H1W	−0.094 (8)	0.159 (4)	1.036 (3)	0.048 (11)*
H2W	0.100 (8)	0.180 (4)	1.120 (3)	0.062 (12)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na1	0.0363 (7)	0.0395 (6)	0.0280 (6)	0.0220 (5)	0.0043 (5)	0.0049 (5)
O11	0.0377 (12)	0.0496 (13)	0.0327 (11)	0.0314 (11)	0.0144 (9)	0.0189 (10)

O21	0.0310 (11)	0.0478 (12)	0.0261 (10)	0.0229 (10)	0.0094 (8)	0.0109 (9)
O31	0.0457 (13)	0.0432 (12)	0.0326 (11)	0.0314 (11)	0.0027 (9)	0.0024 (9)
O41	0.0262 (10)	0.0371 (10)	0.0272 (10)	0.0172 (8)	0.0049 (8)	0.0079 (8)
C11	0.0224 (13)	0.0319 (14)	0.0231 (13)	0.0154 (11)	0.0066 (10)	0.0075 (11)
C21	0.0410 (19)	0.060 (2)	0.0282 (15)	0.0316 (17)	−0.0022 (13)	−0.0032 (14)
C31	0.053 (2)	0.070 (2)	0.0358 (16)	0.044 (2)	0.0250 (15)	0.0303 (16)
C41	0.0183 (13)	0.0272 (13)	0.0280 (14)	0.0091 (11)	0.0066 (10)	0.0109 (11)
C51	0.0212 (13)	0.0303 (14)	0.0255 (13)	0.0108 (11)	0.0085 (10)	0.0097 (11)
O12	0.0395 (13)	0.0502 (13)	0.0555 (14)	0.0281 (11)	0.0011 (10)	0.0165 (11)
O22	0.0478 (15)	0.0680 (17)	0.0428 (14)	0.0312 (13)	−0.0117 (11)	−0.0049 (12)
O32	0.0443 (13)	0.0446 (12)	0.0435 (12)	0.0315 (11)	0.0059 (10)	0.0105 (10)
O42	0.0428 (13)	0.0451 (13)	0.0444 (13)	0.0241 (11)	0.0043 (10)	−0.0080 (10)
C12	0.0242 (14)	0.0278 (13)	0.0271 (13)	0.0128 (11)	0.0062 (11)	0.0074 (11)
C22	0.047 (2)	0.0526 (19)	0.0301 (15)	0.0300 (17)	0.0129 (13)	0.0122 (14)
C32	0.0409 (18)	0.0261 (14)	0.0410 (17)	0.0140 (13)	−0.0002 (14)	0.0031 (12)
C42	0.0238 (14)	0.0378 (15)	0.0360 (15)	0.0105 (13)	0.0059 (12)	0.0104 (13)
C52	0.0249 (15)	0.0298 (14)	0.0362 (15)	0.0106 (12)	0.0115 (12)	0.0082 (12)
O1W	0.0357 (13)	0.0374 (12)	0.0376 (12)	0.0202 (11)	0.0037 (10)	0.0063 (10)

Geometric parameters (Å, º)

Na1—O42	2.261 (2)	C21—C31	1.464 (5)
Na1—O21^i	2.325 (2)	C21—H21A	0.97
Na1—O41^i	2.370 (2)	C21—H21B	0.97
Na1—O41^{ii}	2.384 (2)	C31—H31A	0.97
Na1—O1W	2.526 (3)	C31—H31B	0.97
Na1—O21	2.533 (2)	O12—C42	1.215 (3)
Na1—Na1^{iii}	3.245 (2)	O22—C42	1.298 (4)
Na1—Na1^i	3.769 (3)	O22—H22	0.93 (6)
O11—C41	1.320 (3)	O32—C52	1.233 (3)
O11—H11	0.77 (5)	O42—C52	1.258 (3)
O21—C41	1.204 (3)	C12—C42	1.491 (4)
O21—Na1^i	2.325 (2)	C12—C52	1.504 (4)
O31—C51	1.301 (3)	C12—C32	1.518 (4)
O31—H31	0.72 (6)	C12—C22	1.520 (4)
O41—C51	1.207 (3)	C22—C32	1.451 (5)
O41—Na1^i	2.370 (2)	C22—H22A	0.97
O41—Na1^{iv}	2.384 (2)	C22—H22B	0.97
C11—C41	1.491 (3)	C32—H32A	0.97
C11—C51	1.503 (3)	C32—H32B	0.97
C11—C21	1.513 (4)	O1W—H1W	0.85 (4)
C11—C31	1.525 (4)	O1W—H2W	0.86 (4)
O42—Na1—O21^i	89.54 (9)	C21—C31—H31B	117.7
O42—Na1—O41^i	163.78 (9)	C11—C31—H31B	117.7
O21^i—Na1—O41^i	74.26 (8)	H31A—C31—H31B	114.8
O42—Na1—O41^{ii}	101.48 (9)	O21—C41—O11	122.1 (2)
O21^i—Na1—O41^{ii}	155.79 (9)	O21—C41—C11	125.7 (2)

O41^i—Na1—O41^{ii}	93.90 (7)	O11—C41—C11	112.2 (2)
O42—Na1—O1W	91.34 (9)	O41—C51—O31	124.8 (2)
O21^i—Na1—O1W	89.24 (9)	O41—C51—C11	124.1 (2)
O41^i—Na1—O1W	87.70 (8)	O31—C51—C11	110.9 (2)
O41^{ii}—Na1—O1W	111.72 (9)	C42—O22—H22	109 (4)
O42—Na1—O21	95.42 (9)	C52—O42—Na1	142.02 (19)
O21^i—Na1—O21	78.33 (8)	C42—C12—C52	119.5 (2)
O41^i—Na1—O21	82.32 (8)	C42—C12—C32	116.4 (2)
O41^{ii}—Na1—O21	79.21 (8)	C52—C12—C32	116.0 (2)
O1W—Na1—O21	165.77 (8)	C42—C12—C22	116.4 (2)
C41—O11—H11	108 (4)	C52—C12—C22	116.4 (2)
C41—O21—Na1^i	122.87 (17)	C32—C12—C22	57.1 (2)
C41—O21—Na1	118.33 (18)	C32—C22—C12	61.39 (19)
Na1^i—O21—Na1	101.67 (8)	C32—C22—H22A	117.6
C51—O31—H31	113 (4)	C12—C22—H22A	117.6
C51—O41—Na1^i	130.55 (17)	C32—C22—H22B	117.6
C51—O41—Na1^{iv}	142.66 (17)	C12—C22—H22B	117.6
Na1^i—O41—Na1^{iv}	86.10 (7)	H22A—C22—H22B	114.7
C41—C11—C51	119.0 (2)	C22—C32—C12	61.5 (2)
C41—C11—C21	115.9 (2)	C22—C32—H32A	117.6
C51—C11—C21	117.8 (2)	C12—C32—H32A	117.6
C41—C11—C31	116.9 (2)	C22—C32—H32B	117.6
C51—C11—C31	114.9 (2)	C12—C32—H32B	117.6
C21—C11—C31	57.6 (2)	H32A—C32—H32B	114.7
C31—C21—C11	61.6 (2)	O12—C42—O22	121.9 (3)
C31—C21—H21A	117.6	O12—C42—C12	121.9 (3)
C11—C21—H21A	117.6	O22—C42—C12	116.1 (2)
C31—C21—H21B	117.6	O32—C52—O42	124.4 (3)
C11—C21—H21B	117.6	O32—C52—C12	118.3 (2)
H21A—C21—H21B	114.7	O42—C52—C12	117.2 (2)
C21—C31—C11	60.8 (2)	Na1—O1W—H1W	99 (2)
C21—C31—H31A	117.7	Na1—O1W—H2W	129 (3)
C11—C31—H31A	117.7	H1W—O1W—H2W	100 (4)
O42—Na1—O21—C41	49.41 (19)	C21—C11—C51—O41	−172.1 (3)
O21^i—Na1—O21—C41	137.8 (2)	C31—C11—C51—O41	122.9 (3)
O41^i—Na1—O21—C41	−146.76 (18)	C41—C11—C51—O31	160.1 (2)
O41^{ii}—Na1—O21—C41	−51.28 (18)	C21—C11—C51—O31	11.0 (4)
O1W—Na1—O21—C41	167.4 (3)	C31—C11—C51—O31	−54.0 (3)
Na1^{iii}—Na1—O21—C41	−99.11 (18)	O21^i—Na1—O42—C52	−167.9 (4)
Na1^i—Na1—O21—C41	137.8 (2)	O41^i—Na1—O42—C52	−170.7 (3)
O42—Na1—O21—Na1^i	−88.41 (9)	O41^{ii}—Na1—O42—C52	−9.6 (4)
O41^i—Na1—O21—Na1^i	75.43 (8)	O1W—Na1—O42—C52	102.9 (4)
O41^{ii}—Na1—O21—Na1^i	170.91 (9)	O21—Na1—O42—C52	−89.7 (4)
O1W—Na1—O21—Na1^i	29.6 (3)	Na1^{iii}—Na1—O42—C52	−16.7 (5)
Na1^{iii}—Na1—O21—Na1^i	123.07 (8)	Na1^i—Na1—O42—C52	−126.9 (4)
C41—C11—C21—C31	106.7 (3)	C42—C12—C22—C32	105.6 (3)
C51—C11—C21—C31	−103.3 (3)	C52—C12—C22—C32	−105.2 (3)

C41—C11—C31—C21	−105.0 (3)	C42—C12—C32—C22	−105.7 (3)
C51—C11—C31—C21	108.4 (3)	C52—C12—C32—C22	105.8 (3)
Na1^i—O21—C41—O11	−135.2 (2)	C52—C12—C42—O12	177.4 (3)
Na1—O21—C41—O11	96.4 (3)	C32—C12—C42—O12	30.1 (4)
Na1^i—O21—C41—C11	47.5 (3)	C22—C12—C42—O12	−34.4 (4)
Na1—O21—C41—C11	−80.9 (3)	C52—C12—C42—O22	−3.1 (4)
C51—C11—C41—O21	−1.4 (4)	C32—C12—C42—O22	−150.4 (3)
C21—C11—C41—O21	148.3 (3)	C22—C12—C42—O22	145.1 (3)
C31—C11—C41—O21	−146.7 (3)	Na1—O42—C52—O32	11.3 (6)
C51—C11—C41—O11	−178.9 (2)	Na1—O42—C52—C12	−170.4 (2)
C21—C11—C41—O11	−29.3 (3)	C42—C12—C52—O32	−179.7 (3)
C31—C11—C41—O11	35.8 (3)	C32—C12—C52—O32	−32.3 (4)
Na1^i—O41—C51—O31	173.4 (2)	C22—C12—C52—O32	32.0 (4)
Na1^{iv}—O41—C51—O31	6.5 (5)	C42—C12—C52—O42	1.9 (4)
Na1^i—O41—C51—C11	−3.1 (4)	C32—C12—C52—O42	149.3 (3)
Na1^{iv}—O41—C51—C11	−170.0 (2)	C22—C12—C52—O42	−146.4 (3)
C41—C11—C51—O41	−23.0 (4)		

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

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O22—H22⋯O42	0.93 (6)	1.56 (6)	2.429 (3)	154 (5)
O1W—H2W⋯O12^v	0.86 (4)	1.90 (4)	2.737 (3)	162 (4)
O1W—H1W⋯O22^{ii}	0.85 (4)	1.98 (4)	2.777 (4)	155 (3)
O11—H11⋯O1W^{iii}	0.77 (5)	1.88 (5)	2.642 (3)	170 (5)
O31—H31⋯O32^{iv}	0.72 (6)	1.80 (6)	2.478 (3)	155 (6)

Symmetry codes: (ii) x−1, y, z; (iii) −x, −y+1, −z+2; (iv) x+1, y, z; (v) −x+1, −y, −z+2.