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Poly[diaquabis(μ-hydrogen benzene-1,2,4-tricarboxylato)copper(II)disodium]: a novel 4,5,6-connected trinodal net

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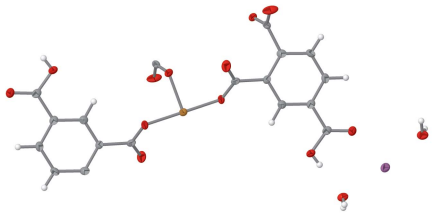
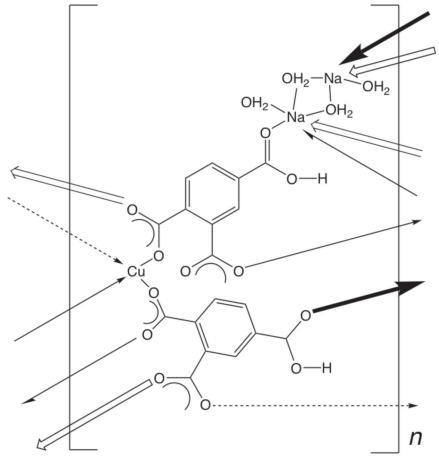
In the title compound, $[CuNa_2(C_9H_4O_6)_2(H_2O)_4]_n$, the Cu^{II} cations are square-planar coordinated by carboxylate O-atom donors from four different hydrogen benzene-1,2,4-tricarboxylate (btcH) ligands, thereby forming $[Cu(btcH)_2]_n^{2n-}$ coordination polymer ribbons. These are connected by octahedrally coordinated and hydrated Na^{I} cations within $Na_2(\mu\text{-}H_2O)_2$ clusters to construct the full $[Na_2(H_2O)_4Cu(btcH)_2]_n$ three-dimensional coordination polymer.

3D view



Chemical scheme



Structure description

The title coordination polymer was isolated during an attempt to prepare a copper benzene-1,2,4-tricarboxylate (btc) coordination polymer containing *N*,*N*′-bis(pyridin-3-ylmethyl)piperazine (3-bpmp) ligands. The 3-bpmp ligand has been used to construct coordination polymers with rare topologies, such as the $(4^46^2)(4^46^6)$ **tcs** topology in $\{[Zn_2(\text{hydrogen pyromellitate})_2(H_2O)_2(H_2\text{-3-bpmp})]\cdot H_2O\}_n$ (Blake *et al.*, 2011).

The asymmetric unit of the title compound contains a Cu^{II} cation on a crystallographic inversion center, a protonated hydrogen benzene-1,2,4-tricarboxylate (btcH) ligand, an Na^{I} cation on a general position, and two aqua ligands bound to the Na atom. Operation of the inversion center affords a square-planar coordination geometry at the Cu^{II} cation, ligated by carboxylate O-atom donors from four different btcH ligands. The Na atom is coordinated in an octahedral geometry, with a *mer* disposition of three bound water molecules and a *mer* disposition of carboxylate O-atom donors from three different btcH ligands. A depiction of the coordination geometries and btcH ligand is shown in Fig. 1. Bond lengths and angles within the coordination spheres at Cu^{II} and Na^{I} are listed in Table 1.

The Cu^{II} cations are conjoined by pairs of btcH ligands *via* their deprotonated carboxylate termini to construct anionic $[Cu(btcH)_2]_n^{2n-}$ coordination polymer ribbons oriented parallel to [100] (Fig. 2). Within the $[Cu(btcH)_2]_n^{2n-}$ ribbons, the Cu···Cu

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.944 (2)	Na1—O3^{v}	2.413 (3)
Cu1—O1^{i}	1.944 (2)	Na1—O5	2.390 (2)
Cu1—O3^{ii}	1.9681 (19)	Na1—O7	2.473 (3)
Cu1—O3^{iii}	1.9681 (19)	Na1—O8	2.354 (3)
Na1—O2^{iv}	2.571 (3)	Na1—O8^{vi}	2.413 (3)
O1—Cu1—O1^{i}	180	O5—Na1—O8^{vi}	150.41 (10)
O1^{i}—Cu1—O3^{iii}	87.13 (9)	O7—Na1—O2^{iv}	96.31 (10)
O1^{i}—Cu1—O3^{ii}	92.88 (9)	O8^{vi}—Na1—O2^{iv}	66.08 (9)
O1—Cu1—O3^{iii}	92.87 (9)	O8—Na1—O2^{iv}	72.51 (9)
O1—Cu1—O3^{ii}	87.13 (9)	O8—Na1—O3^{v}	115.87 (9)
O3^{iii}—Cu1—O3^{ii}	180.00 (14)	O8^{vi}—Na1—O3^{v}	97.25 (9)
O3^{v}—Na1—O2^{iv}	162.81 (9)	O8—Na1—O5	89.37 (9)
O3^{v}—Na1—O7	77.27 (10)	O8—Na1—O7	165.87 (11)
O5—Na1—O2^{iv}	89.20 (8)	O8^{vi}—Na1—O7	85.02 (9)
O5—Na1—O3^{v}	105.37 (9)	O8—Na1—O8^{vi}	97.79 (8)
O5—Na1—O7	81.70 (9)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6···O7	0.70 (4)	1.91 (4)	2.613 (3)	177 (5)
O7—H7A···O4^{iv}	0.68 (4)	2.01 (4)	2.685 (4)	169 (4)
O7—H7B···O1^{vii}	0.81 (5)	2.02 (5)	2.816 (4)	168 (4)
O8—H8A···O4^{viii}	0.84 (2)	1.90 (2)	2.736 (3)	170 (4)
O8—H8B···O2^{ix}	0.81 (2)	2.54 (3)	2.720 (3)	94 (3)

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

internuclear distance of 6.9035 (7) Å coincides with the *a* lattice parameter. The protonated carboxylate groups of the btcH ligands project towards the periphery of the ribbon motifs.

Pairs of bridging water molecules create cationic $Na_2(\mu\text{-}H_2O)_2^{2+}$ clusters with an Na···Na distance of 3.140 (5) Å (Fig. 3). These clusters conjoin adjacent anionic $[Cu(btcH)_2]_n^{2n-}$ ribbons into an $[Na_2(H_2O)_4Cu(btcH)_2]_n$ three-dimensional coordination polymer network (Fig. 4). Ancillary

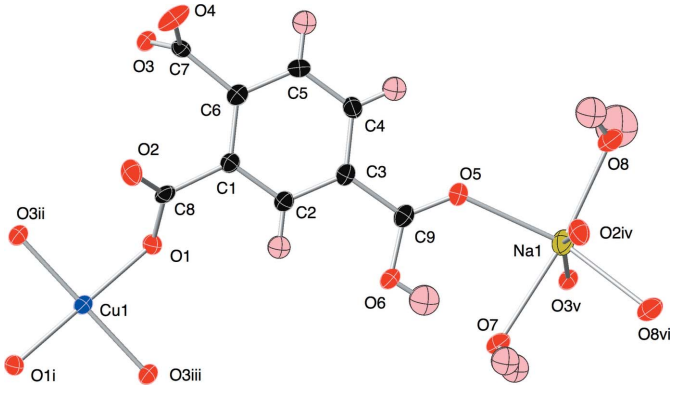


Figure 1
The coordination environments within the title compound, showing the octahedral coordination at the Na^{I} cation and the square-planar coordination at the Cu^{II} cation. Displacement ellipsoids are drawn at the 50% probability level.Symmetry codes are as listed in Table 2.

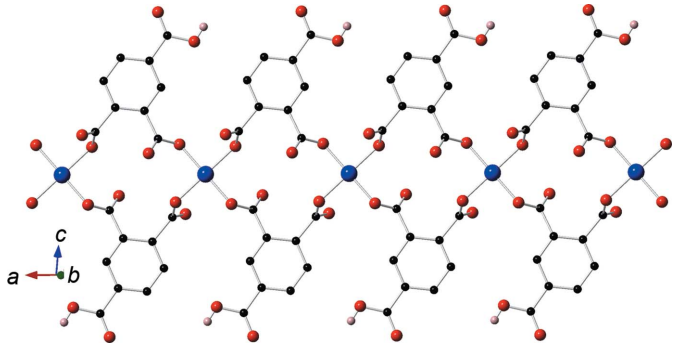


Figure 2
$[Cu(btcH)_2]_n^{2n-}$ coordination polymer ribbon parallel to [100] in the title compound.

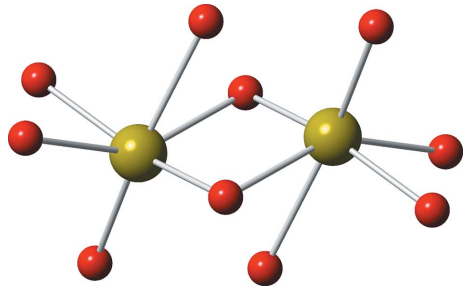


Figure 3
Cationic $Na_2(\mu\text{-}H_2O)_2^{2+}$ cluster in the title compound.

structural stabilization is provided by hydrogen bonding between the protonated btcH carboxylate group and non-bridging water molecules bound to the Na^{I} cations (Table 2).

Treating the Cu^{II} atoms as 4-connected nodes, the btcH ligands as 5-connected nodes, and the $Na_2(\mu\text{-}H_2O)_2^{2+}$ clusters as 6-connected nodes results in a 4,5,6-connected $\{4^2.8^4\}\{4^6.6^6.8^3\}\{4^8.6^2\}_2$ topology (Fig. 5) for the underlying network of the $[Na_2(H_2O)_4Cu(btcH)_2]_n$ three-dimensional

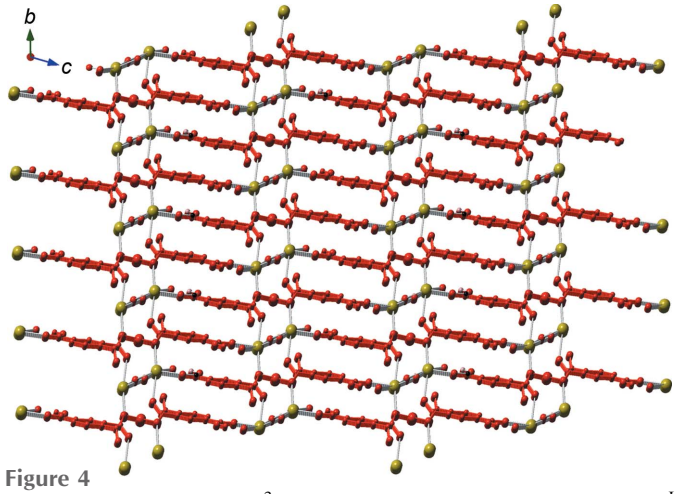


Figure 4
Connection of $[Cu(btcH)_2]_n^{2n-}$ coordination polymer ribbons by Na^{I} cations to construct the $[Na_2(H_2O)_4Cu(btcH)_2]_n$ three-dimensional coordination polymer structure of the title compound. Individual $[Cu(btcH)_2]_n^{2n-}$ ribbons are drawn in red.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[CuNa_2(C_9H_4O_6)_2(H_2O)_4]$
M_r	597.83
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	173
a, b, c (Å)	6.9048 (9), 7.0555 (9), 11.8449 (15)
α, β, γ (°)	105.071 (2), 93.073 (2), 109.955 (2)
V (Å^3)	517.26 (11)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.19
Crystal size (mm)	0.26 × 0.08 × 0.03
Data collection	
Diffractometer	Bruker SMART CCD 1K area detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2015)
T_{min}, T_{max}	0.659, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4640, 1906, 1606
R_{int}	0.031
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.603
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.099, 1.07
No. of reflections	1906
No. of parameters	199
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.48, −0.35

Computer programs: COSMO (Bruker, 2009), *SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) within *OLEX2* (Dolomanov *et al.*, 2009) and *Crystal Maker* (Palmer, 2018).

coordination polymer, as determined by *TOPOS* (Blatov *et al.*, 2014).

Synthesis and crystallization

$Cu(NO_3)_2{\cdot}2.5H_2O$ (86 mg, 0.37 mmol), benzene-1,2,4-tricarboxylic acid (78 mg, 0.37 mol), *N*,*N*′-bis(pyridin-3-ylmethyl)-piperazine (99 mg, 0.37 mol) and 0.75 ml of a 1.0 *M* NaOH solution were placed in 10 ml distilled H_2O in a Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 393 K for 24 h, and then cooled slowly to 278 K. Blue crystals of the title compound (47 mg, 21% yield based on copper) were isolated after washing with distilled water and acetone, and drying in air.

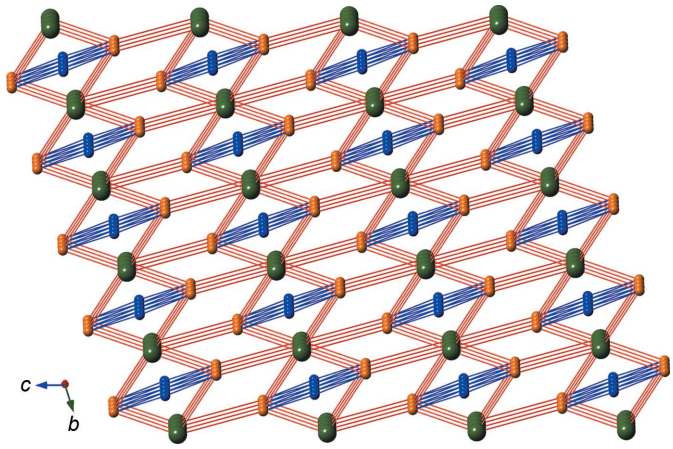


Figure 5
Schematic perspective of the 4,5,6-connected $\{4^2.8^4\}\{4^6.6^6.8^3\}\{4^8.6^2\}_2$ topology network of the $[Na_2(H_2O)_4Cu(btcH)_2]_n$ three-dimensional coordination polymer within the title compound. The 4-connected Cu^{II} atom nodes are depicted as blue spheres. The 5-connected btcH ligand nodes are depicted as orange spheres. The 6-connected $Na_2(\mu\text{-}H_2O)_2^{2+}$ cluster modes are depicted as green spheres.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

Funding information

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full crystallographic data

IUCrData (2018). **3**, x180676 [https://doi.org/10.1107/S2414314618006764]

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Crystal data

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M_r = 597.83
Triclinic, $P\overline{1}$
a = 6.9048 (9) Å
b = 7.0555 (9) Å
c = 11.8449 (15) Å
α = 105.071 (2)°
β = 93.073 (2)°
γ = 109.955 (2)°
V = 517.26 (11) Å^3
Z = 1
$F(000)$ = 301
D_x = 1.913 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2453 reflections
θ = 3.2–25.4°
μ = 1.19 mm^{-1}
T = 173 K
Needle, blue
0.26 × 0.08 × 0.03 mm

Data collection

Bruker SMART CCD 1K area detector diffractometer
Radiation source: sealed X-ray tube
Graphite monochromator
Detector resolution: 7.9 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2015)
T_{min} = 0.659, T_{max} = 0.745
4640 measured reflections
1906 independent reflections
1606 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 25.4°, θ_{min} = 1.8°
h = −8→8
k = −8→8
l = −13→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.099
S = 1.07
1906 reflections
199 parameters
3 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 0.245P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Special details

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

Refinement. The structure was refined by Least Squares using version 2014/6 of XL (Sheldrick, 2015b) incorporated in Olex2 (Dolomanov *et al.*, 2009). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model, except for the Hydrogen atom on the oxygen atoms which was found by difference Fourier methods and refined isotropically.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.0000	0.5000	0.0000	0.01725 (19)
Na1	0.38930 (19)	0.8360 (2)	0.87662 (11)	0.0247 (3)
O1	0.2019 (3)	0.5155 (3)	0.12631 (18)	0.0188 (5)
O2	0.4758 (4)	0.7631 (4)	0.09054 (19)	0.0265 (6)
O3	0.8109 (3)	0.5155 (3)	0.11767 (18)	0.0181 (5)
O4	0.9730 (4)	0.8616 (4)	0.1695 (2)	0.0322 (6)
O5	0.4966 (4)	0.7908 (4)	0.68605 (19)	0.0248 (6)
O6	0.2072 (4)	0.7132 (4)	0.5602 (2)	0.0242 (6)
H6	0.167 (7)	0.722 (7)	0.614 (4)	0.039 (13)*
O7	0.0503 (4)	0.7544 (5)	0.7571 (2)	0.0221 (6)
H7A	0.032 (6)	0.846 (6)	0.770 (3)	0.021 (12)*
H7B	−0.036 (7)	0.673 (7)	0.783 (4)	0.038 (12)*
O8	0.7418 (4)	0.9752 (4)	0.9649 (2)	0.0264 (6)
H8A	0.836 (5)	1.038 (5)	0.931 (3)	0.028*
H8B	0.770 (5)	0.877 (4)	0.973 (3)	0.028*
C1	0.5084 (5)	0.6815 (5)	0.2697 (3)	0.0143 (6)
C2	0.7216 (5)	0.7167 (5)	0.2844 (3)	0.0162 (7)
C3	0.8280 (5)	0.7616 (5)	0.3969 (3)	0.0188 (7)
H3	0.965 (6)	0.780 (5)	0.411 (3)	0.020 (9)*
C4	0.7268 (5)	0.7724 (5)	0.4942 (3)	0.0192 (7)
H4	0.806 (5)	0.811 (5)	0.574 (3)	0.027 (10)*
C5	0.5150 (5)	0.7383 (5)	0.4802 (3)	0.0166 (7)
C6	0.4076 (5)	0.6917 (5)	0.3678 (3)	0.0170 (7)
H6A	0.259 (5)	0.667 (5)	0.358 (2)	0.011 (8)*
C7	0.3906 (5)	0.6523 (5)	0.1510 (3)	0.0170 (7)
C8	0.8432 (5)	0.7000 (5)	0.1818 (3)	0.0168 (7)
C9	0.4075 (5)	0.7501 (5)	0.5861 (3)	0.0185 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0163 (3)	0.0219 (3)	0.0148 (3)	0.0074 (2)	0.0044 (2)	0.0065 (2)
Na1	0.0207 (7)	0.0273 (8)	0.0196 (7)	0.0028 (6)	0.0047 (6)	0.0038 (6)
O1	0.0145 (12)	0.0263 (13)	0.0133 (11)	0.0032 (10)	0.0001 (9)	0.0083 (9)
O2	0.0271 (14)	0.0285 (14)	0.0205 (12)	0.0020 (11)	0.0016 (10)	0.0131 (11)
O3	0.0180 (12)	0.0211 (13)	0.0141 (11)	0.0060 (10)	0.0045 (9)	0.0045 (9)

O4	0.0325 (15)	0.0225 (13)	0.0456 (16)	0.0085 (12)	0.0266 (12)	0.0148 (11)
O5	0.0221 (13)	0.0342 (14)	0.0159 (13)	0.0084 (11)	0.0031 (10)	0.0067 (10)
O6	0.0214 (14)	0.0392 (15)	0.0161 (13)	0.0144 (12)	0.0080 (11)	0.0095 (11)
O7	0.0241 (14)	0.0211 (14)	0.0246 (14)	0.0096 (12)	0.0104 (11)	0.0092 (11)
O8	0.0256 (14)	0.0350 (16)	0.0280 (13)	0.0152 (12)	0.0114 (11)	0.0181 (12)
C1	0.0179 (16)	0.0127 (15)	0.0137 (15)	0.0060 (13)	0.0031 (12)	0.0052 (12)
C2	0.0173 (16)	0.0130 (16)	0.0208 (17)	0.0054 (13)	0.0064 (13)	0.0086 (13)
C3	0.0132 (17)	0.0218 (18)	0.0221 (17)	0.0067 (14)	0.0022 (13)	0.0072 (14)
C4	0.0193 (18)	0.0186 (17)	0.0166 (17)	0.0041 (14)	−0.0008 (14)	0.0047 (14)
C5	0.0202 (17)	0.0134 (16)	0.0159 (16)	0.0047 (13)	0.0039 (13)	0.0057 (13)
C6	0.0169 (17)	0.0150 (16)	0.0179 (17)	0.0053 (13)	0.0026 (13)	0.0040 (13)
C7	0.0190 (18)	0.0204 (17)	0.0162 (16)	0.0114 (14)	0.0074 (13)	0.0068 (13)
C8	0.0138 (16)	0.0207 (18)	0.0179 (16)	0.0072 (14)	0.0017 (13)	0.0081 (14)
C9	0.0224 (18)	0.0156 (16)	0.0177 (17)	0.0062 (14)	0.0064 (14)	0.0055 (13)

Geometric parameters (Å, º)

Cu1—O1	1.944 (2)	O6—H6	0.70 (4)
Cu1—O1^{i}	1.944 (2)	O6—C9	1.320 (4)
Cu1—O3^{ii}	1.9681 (19)	O7—H7A	0.68 (4)
Cu1—O3^{iii}	1.9681 (19)	O7—H7B	0.81 (5)
Na1—O2^{iv}	2.571 (3)	O8—Na1^{vi}	2.413 (3)
Na1—O3^{v}	2.413 (3)	O8—H8A	0.842 (18)
Na1—O5	2.390 (2)	O8—H8B	0.808 (18)
Na1—O7	2.473 (3)	C1—C2	1.400 (4)
Na1—O8	2.354 (3)	C1—C6	1.385 (4)
Na1—O8^{vi}	2.413 (3)	C1—C7	1.514 (4)
O1—C7	1.292 (4)	C2—C3	1.389 (4)
O2—Na1^{vii}	2.787 (3)	C2—C8	1.516 (4)
O2—Na1^{iv}	2.571 (3)	C3—H3	0.91 (4)
O2—C7	1.222 (4)	C3—C4	1.379 (4)
O3—Cu1^{viii}	1.9681 (19)	C4—H4	0.99 (4)
O3—Na1^{v}	2.413 (3)	C4—C5	1.392 (4)
O3—C8	1.261 (4)	C5—C6	1.390 (4)
O4—C8	1.236 (4)	C5—C9	1.489 (4)
O5—C9	1.219 (4)	C6—H6A	0.98 (3)
O1—Cu1—O1^{i}	180.0	Na1—O8—Na1^{vi}	82.21 (8)
O1^{i}—Cu1—O3^{iii}	87.13 (9)	Na1^{vi}—O8—H8A	122 (2)
O1^{i}—Cu1—O3^{ii}	92.88 (9)	Na1—O8—H8A	121 (3)
O1—Cu1—O3^{iii}	92.87 (9)	Na1—O8—H8B	107 (3)
O1—Cu1—O3^{ii}	87.13 (9)	Na1^{vi}—O8—H8B	118 (3)
O3^{iii}—Cu1—O3^{ii}	180.00 (14)	H8A—O8—H8B	105 (3)
O3^{v}—Na1—O2^{iv}	162.81 (9)	C2—C1—C7	121.4 (3)
O3^{v}—Na1—O7	77.27 (10)	C6—C1—C2	119.1 (3)
O5—Na1—O2^{iv}	89.20 (8)	C6—C1—C7	119.3 (3)
O5—Na1—O3^{v}	105.37 (9)	C1—C2—C8	122.9 (3)
O5—Na1—O7	81.70 (9)	C3—C2—C1	119.5 (3)

O5—Na1—O8^{vi}	150.41 (10)	C3—C2—C8	117.5 (3)
O7—Na1—O2^{iv}	96.31 (10)	C2—C3—H3	123 (2)
O8^{vi}—Na1—O2^{iv}	66.08 (9)	C4—C3—C2	121.0 (3)
O8—Na1—O2^{iv}	72.51 (9)	C4—C3—H3	116 (2)
O8—Na1—O3^{v}	115.87 (9)	C3—C4—H4	120 (2)
O8^{vi}—Na1—O3^{v}	97.25 (9)	C3—C4—C5	119.8 (3)
O8—Na1—O5	89.37 (9)	C5—C4—H4	120 (2)
O8—Na1—O7	165.87 (11)	C4—C5—C9	119.2 (3)
O8^{vi}—Na1—O7	85.02 (9)	C6—C5—C4	119.4 (3)
O8—Na1—O8^{vi}	97.79 (8)	C6—C5—C9	121.3 (3)
C7—O1—Cu1	122.27 (19)	C1—C6—C5	121.1 (3)
Na1^{iv}—O2—Na1^{vii}	71.48 (7)	C1—C6—H6A	119.4 (17)
C7—O2—Na1^{iv}	132.9 (2)	C5—C6—H6A	119.5 (17)
C7—O2—Na1^{vii}	139.5 (2)	O1—C7—C1	115.1 (3)
Cu1^{viii}—O3—Na1^{v}	109.41 (9)	O2—C7—O1	126.2 (3)
C8—O3—Cu1^{viii}	114.38 (19)	O2—C7—C1	118.6 (3)
C8—O3—Na1^{v}	135.22 (19)	O3—C8—C2	116.0 (3)
C9—O5—Na1	133.8 (2)	O4—C8—O3	124.3 (3)
C9—O6—H6	107 (4)	O4—C8—C2	119.6 (3)
Na1—O7—H7A	106 (3)	O5—C9—O6	123.9 (3)
Na1—O7—H7B	106 (3)	O5—C9—C5	123.1 (3)
H7A—O7—H7B	107 (4)	O6—C9—C5	113.0 (3)

Cu1^{ix}—Na1—O5—C9	59.0 (3)	O8—Na1—O5—C9	−168.1 (3)
Cu1^{ix}—Na1—O8—Na1^{vi}	−66.87 (8)	O8^{vi}—Na1—O5—C9	−63.3 (4)
Cu1—O1—C7—O2	−12.0 (4)	O8^{vi}—Na1—O8—Na1^{vi}	0.0
Cu1—O1—C7—C1	164.65 (18)	C1—C2—C3—C4	−0.1 (5)
Cu1^{viii}—O3—C8—O4	4.1 (4)	C1—C2—C8—O3	−74.2 (4)
Cu1^{viii}—O3—C8—C2	−171.8 (2)	C1—C2—C8—O4	109.7 (4)
Na1^{vii}—Cu1—O1—C7	12.9 (2)	C2—C1—C6—C5	0.7 (5)
Na1^{x}—Cu1—O1—C7	−167.1 (2)	C2—C1—C7—O1	143.0 (3)
Na1^{vi}—Na1—O5—C9	−138.8 (3)	C2—C1—C7—O2	−40.1 (4)
Na1^{iv}—O2—C7—O1	114.2 (3)	C2—C3—C4—C5	−0.1 (5)
Na1^{vii}—O2—C7—O1	−0.6 (5)	C3—C2—C8—O3	103.4 (3)
Na1^{iv}—O2—C7—C1	−62.4 (4)	C3—C2—C8—O4	−72.7 (4)
Na1^{vii}—O2—C7—C1	−177.12 (19)	C3—C4—C5—C6	0.6 (5)
Na1^{v}—O3—C8—O4	171.2 (2)	C3—C4—C5—C9	179.9 (3)
Na1^{v}—O3—C8—C2	−4.7 (4)	C4—C5—C6—C1	−1.0 (5)
Na1—O5—C9—O6	−2.0 (5)	C4—C5—C9—O5	0.8 (5)
Na1—O5—C9—C5	177.6 (2)	C4—C5—C9—O6	−179.6 (3)
O1^{i}—Cu1—O1—C7	23 (9)	C6—C1—C2—C3	−0.2 (4)
O2^{ix}—Na1—O5—C9	146.4 (3)	C6—C1—C2—C8	177.4 (3)
O2^{iv}—Na1—O5—C9	−95.6 (3)	C6—C1—C7—O1	−42.6 (4)
O2^{iv}—Na1—O8—Na1^{vi}	61.83 (8)	C6—C1—C7—O2	134.3 (3)
O2^{ix}—Na1—O8—Na1^{vi}	−60.30 (8)	C6—C5—C9—O5	−179.9 (3)
O3^{iii}—Cu1—O1—C7	52.4 (2)	C6—C5—C9—O6	−0.3 (4)
O3^{ii}—Cu1—O1—C7	−127.6 (2)	C7—C1—C2—C3	174.2 (3)
O3^{v}—Na1—O5—C9	75.2 (3)	C7—C1—C2—C8	−8.2 (4)

O3^{v}—Na1—O8—Na1^{vi}	−102.00 (10)	C7—C1—C6—C5	−173.8 (3)
O5—Na1—O8—Na1^{vi}	151.19 (10)	C8—C2—C3—C4	−177.8 (3)
O7—Na1—O5—C9	0.9 (3)	C9—C5—C6—C1	179.8 (3)
O7—Na1—O8—Na1^{vi}	100.6 (4)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6···O7	0.70 (4)	1.91 (4)	2.613 (3)	177 (5)
O7—H7*A*···O4^{iv}	0.68 (4)	2.01 (4)	2.685 (4)	169 (4)
O7—H7*B*···O1^{x}	0.81 (5)	2.02 (5)	2.816 (4)	168 (4)
O8—H8*A*···O4^{xi}	0.84 (2)	1.90 (2)	2.736 (3)	170 (4)
O8—H8*B*···O2^{ix}	0.81 (2)	2.54 (3)	2.720 (3)	94 (3)

Symmetry codes: (iv) −*x*+1, −*y*+2, −*z*+1; (ix) *x*, *y*, *z*+1; (x) −*x*, −*y*+1, −*z*+1; (xi) −*x*+2, −*y*+2, −*z*+1.