metal-organic compounds

Poly[[hexaaquasesqui(μ-benzene-1,2,4,5-tetracarboxylato)dicopper(II)disodium] monohydrate]

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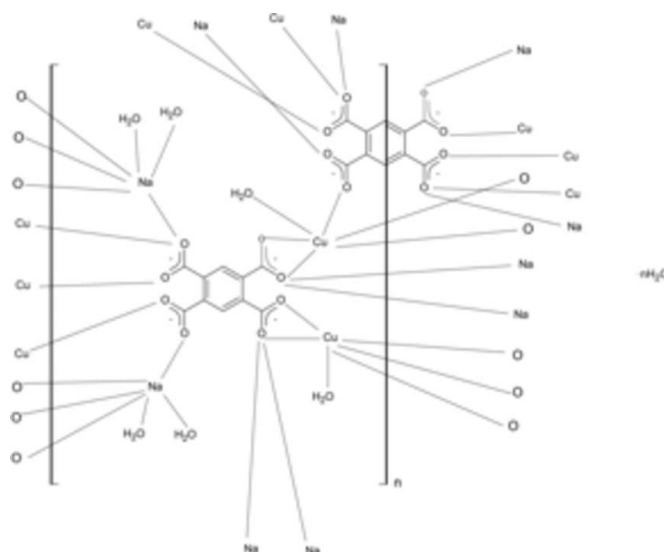Correspondence e-mail: mcamara@univ-zig.sn

In the title compound, $\{[Cu_2Na_2(C_{10}H_2O_8)_{1.5}(H_2O)_6]\cdot H_2O\}_n$, the Cu^{2+} ion is hexacoordinated by five O atoms from benzene-1,2,4,5-tetracarboxylate ($btec^{4-}$) ligands and one water molecule. The Na^+ ion is also hexacoordinated, by four O atoms from $btec^{4-}$ ligands and two water molecules. One of the two $btec^{4-}$ molecules sits on a crystallographic inversion centre. CuO_6 and NaO_6 octahedra are connected, forming bi-dimensional layers. These layers, which extend parallel to the ac plane, are further interconnected by μ_{10}- or μ_{11}-bridging $btec^{4-}$ ligands and by O—H···O hydrogen bonds, involving both $btec^{4-}$ ligands and water molecules, forming a three-dimensional network.

Related literature

For related structures, see: Camara et al. (2013); Luo et al. (2013); Gong & Zhang (2011); Liu et al. (2010); Zhang et al. (2007). For related crystal-growth methods in gels, see: Henisch (1988); Henisch & Roy (1970); Daiguebonne et al. (2003).

Experimental

Crystal data

$[Cu_2Na_2(C_{10}H_2O_8)_{1.5}(H_2O)_6]\cdot H_2O$	V = 2122.66 (6) Å^3
M_r = 674.34	Z = 4
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 8.0844 (1) Å	μ = 2.15 mm^{-1}
b = 16.9103 (3) Å	T = 293 K
c = 15.6815 (3) Å	$0.11 \times 0.08 \times 0.07$ mm
β = 98.055 (1)°	

Data collection

Bruker APEXII diffractometer	34613 measured reflections
Absorption correction: multi-scan	8438 independent reflections
(SADABS; Bruker, 2007)	4356 reflections with $I > 2\sigma(I)$
T_{min} = 0.701, T_{max} = 0.848	R_{int} = 0.058

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049	H atoms treated by a mixture of
$wR(F^2)$ = 0.144	independent and constrained
S = 0.94	refinement
8438 reflections	$\Delta\rho_{max}$ = 1.49 e Å^{-3}
373 parameters	$\Delta\rho_{min}$ = -1.02 e Å^{-3}
15 restraints	

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H42···O112^i	0.81 (2)	1.93 (2)	2.737 (3)	174 (4)
O2—H22···O511	0.82 (2)	1.91 (2)	2.697 (3)	162 (4)
O1—H11···O812	0.80 (2)	1.95 (2)	2.708 (3)	159 (4)
O2—H21···OW1^{ii}	0.78 (2)	1.85 (2)	2.618 (3)	167 (4)
O5—H51···O512^{iii}	0.87 (2)	1.91 (2)	2.744 (3)	161 (4)
O1—H12···O2^{iv}	0.81 (2)	1.99 (2)	2.794 (3)	176 (4)
O3—H32···O1^v	0.85 (2)	2.36 (3)	2.977 (3)	130 (3)

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x - 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $x + 1, y, z$; (v) $-x, y - \frac{1}{2}, -z + \frac{3}{2}$.

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2014 (Sheldrick, 2008); molecular graphics:

DIAMOND (Brandenburg, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supporting information for this paper is available from the IUCr electronic archives (Reference: PK2525).

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supporting information

Poly[[hexaaquasesqui(*μ*-benzene-1,2,4,5-tetracarboxyl-ato)dicopper(II)disodium] monohydrate]

Magatte Camara, Mohamed Fadel Keita, Cherif Cheikh Samsidine Cisse, Carole Daiguebonne and Olivier Guillou

1. Comment

In recent years, much attention has been paid to coordination polymers that involve covalent bonds or supramolecular contacts. A huge number of novel compounds with interesting crystal structures and topologies have been reported. As part of this research, benzene-1,2,4,5-tetracarboxylate (btec^{4-}) can be used as a ligand to form various supramolecular architectures through its four rigid carboxyl groups [*see* Camara *et al.* (2013), Luo *et al.* (2013), Gong & Zhang (2011), Liu *et al.* (2010), Zhang *et al.* (2007)]. In order to enrich this family of compounds, we recently undertook a study devoted to reactions of H$_4$btec with metal ions in gel media. In particular, we were interested in such reactions with agar-agar gel bridges in U-shaped tubes, and we have successfully synthesized a novel polymeric complex from H$_4$btec and copper (II) chloride. We report here the synthesis and the crystal structure of the title coordination polymer. As shown in Fig. 1, the asymmetric unit of the title compound contains two Cu(II) ions, two Na(I) ions, coordinated water molecules and three btec^{4-} ligands. One of the two crystallographically distinct btec^{4-} ligands is located on an inversion centre. One btec^{4-} ligand acts as a m$_{10}$-bridge that links six Cu(II) ions and four Na(I) ions, while the other acts as a m$_{11}$-bridge that links five Cu(II) ions and six Na(I) ions. Cu(II) ions are hexa-coordinated by five O atoms from four btec^{4-} ligands and one O atom from a water molecule, while Na(I) ions are hexa-coordinated by four O atoms from four btec^{4-} ligands and two O atoms from two water molecules. As shown in Fig. 2, two-dimensional Cu–O–Na layers extend parallel to the ac plane. Furthermore, these two-dimensional layers are interconnected by m$_{10}$- or m$_{11}$-bridging btec^{4-} ligands and by O—H⋯O hydrogen bonds, forming a three-dimensional framework.

2. Experimental

All reagents were used as obtained without further purification. Copper (II) chloride was purchased from STREM Chemicals. 1,2,4,5-benzenetetracarboxylic acid was purchased from Acros Organics. Its sodium salt was prepared by addition of four equivalents of sodium hydroxide to a suspension of 1,2,4,5-benzenetetracarboxylic acid in de-ionized water until complete dissolution. Then, the solution was evaporated to dryness. The solid phase was then put in suspension in ethanol, stirred and refluxed for 1 h. After filtration and drying in a desiccator, a white powder of tetra-sodium 1,2,4,5-benzene-tetra-carboxylate was obtained (yield = 90%). Single crystals of the coordination polymer were obtained by slow diffusion of dilute aqueous solutions of Cu(II) chloride (0.25 mmol in 20mL) and of the sodium salt of 1,2,4,5-benzenetetra-carboxylic acid (0.25 mmol in 20mL) through agar-agar gel bridges in U-shaped tubes. The gel was purchased from Acros Organics and gelled according to established procedure [see for example, Henisch *et al.* (1988), Henisch *et al.* (1970), Daiguebonne *et al.* (2003)]. After several weeks, colorless single crystals were obtained.

3. Refinement

The H-atoms from water molecules that could be found in difference maps were included with constrained coordinates. Some hydrogen atoms could not be reliably located, so these have only been taken into account in the formula (*i.e.* not in the model).
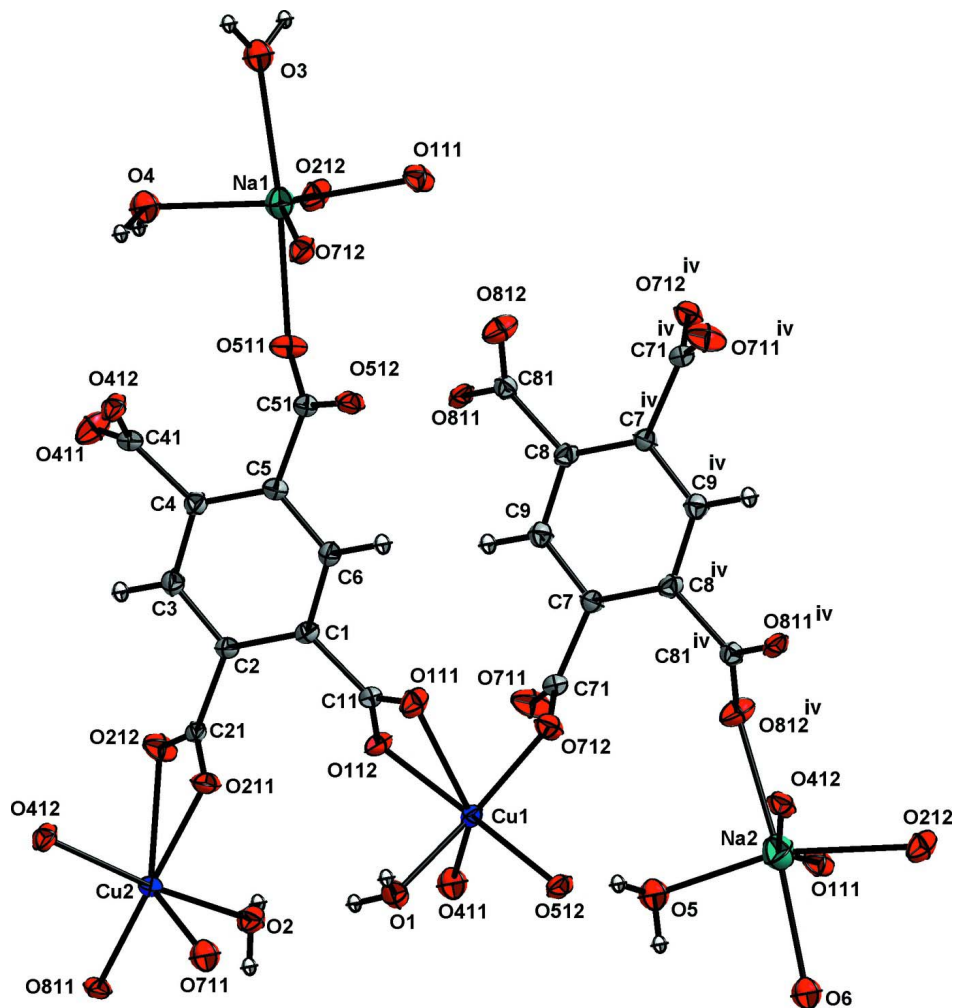
Figure 1

Extended asymetric unit of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (iv) *x*, -*y* + 1/2, *z* - 1/2.]
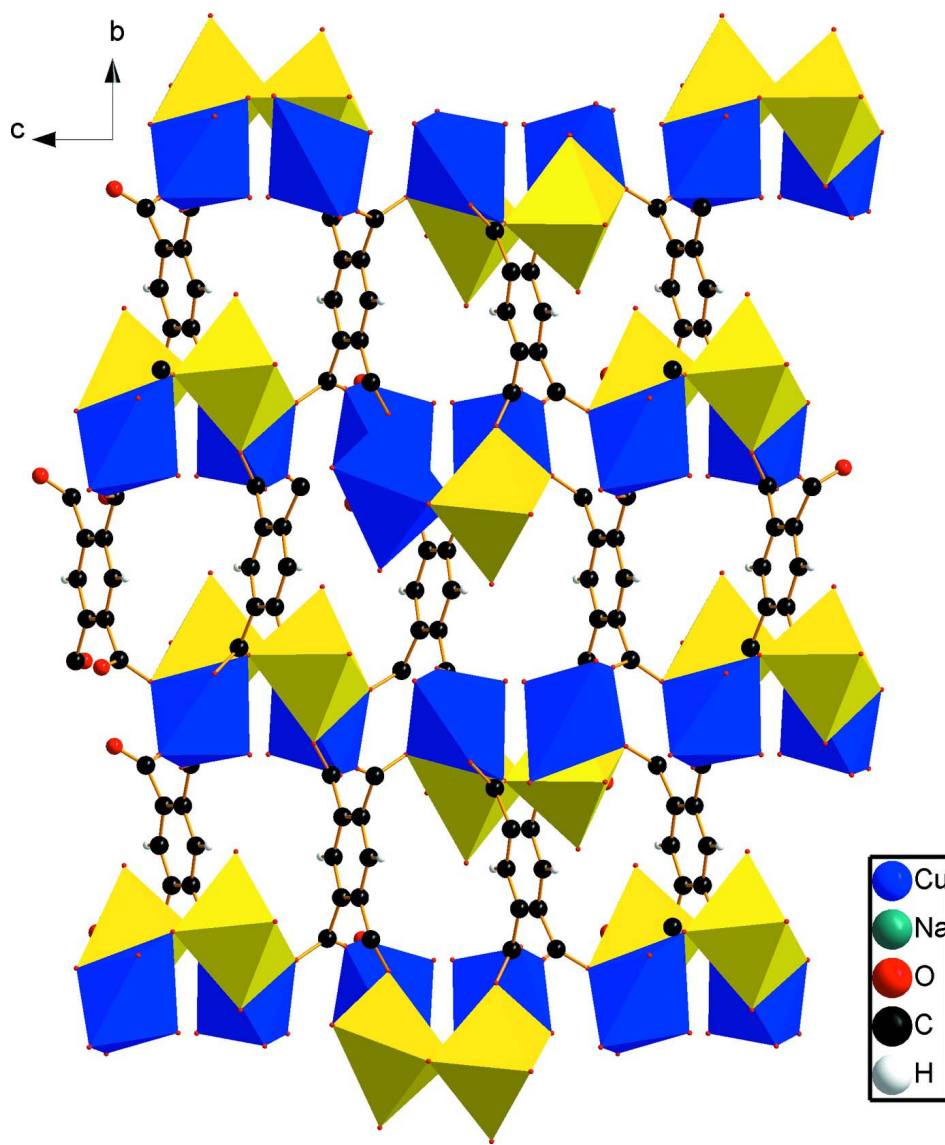
Figure 2
A view of the three-dimensional network of the title compound, projected perpendicular to the *bc*-plane.

Poly[[hexaaquasesqui(μ-benzene-1,2,4,5-tetracarboxylato)dicopper(II)disodium] monohydrate]

Crystal data

$[Cu_2Na_2(C_{10}H_2O_8)_{1.5}(H_2O)_6]·H_2O$
$M_r = 674.34$
Monoclinic, $P2_1/c$
$a = 8.0844 (1)$ Å
$b = 16.9103 (3)$ Å
$c = 15.6815 (3)$ Å
$β = 98.055 (1)°$
$V = 2122.66 (6)$ Å^3
$Z = 4$

$F(000) = 1356$
$D_x = 2.110$ Mg m^{-3}
Mo $Kα$ radiation, $λ = 0.71073$ Å
Cell parameters from 31092 reflections
$θ = 2.9$–$32.0°$
$μ = 2.15$ mm^{-1}
$T = 293$ K
Cobblestone, blue
$0.11 × 0.08 × 0.07$ mm

Data collection

Bruker APEXII diffractometer	34613 measured reflections
Radiation source: Fine-focus sealed tube	8438 independent reflections
Graphite monochromator	4356 reflections with $I > 2\sigma(I)$
CCD rotation images, thin slices scans	$R_{int} = 0.058$
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)	$\theta_{max} = 34.8°$, $\theta_{min} = 3.5°$
$T_{min} = 0.701$, $T_{max} = 0.848$	$h = -11 \rightarrow 12$
	$k = -26 \rightarrow 21$
	$l = -20 \rightarrow 24$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.049$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.144$	
$S = 0.94$	$w = 1/[\sigma^2(F_o^2) + (0.0813P)^2]$
8438 reflections	where $P = (F_o^2 + 2F_c^2)/3$
373 parameters	$(\Delta/\sigma)_{max} = 0.010$
15 restraints	$\Delta\rho_{max} = 1.49$ e Å^{-3}
	$\Delta\rho_{min} = -1.02$ e Å^{-3}

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	$U_{iso}*/U_{eq}$
Cu1	0.15805 (4)	0.25569 (2)	0.80720 (2)	0.01609 (10)
Cu2	−0.45959 (4)	0.26469 (2)	0.54858 (2)	0.01697 (10)
Na1	−0.17322 (14)	0.13536 (7)	0.78727 (8)	0.0284 (3)
Na2	−0.13005 (15)	0.15430 (8)	0.56592 (9)	0.0329 (3)
O112	0.2924 (2)	0.17014 (11)	0.76659 (13)	0.0195 (4)
O211	−0.5911 (2)	0.17609 (11)	0.58371 (13)	0.0215 (4)
O1	0.1863 (2)	0.31650 (12)	0.69877 (13)	0.0224 (4)
O4	−0.4112 (3)	0.11473 (14)	0.85120 (16)	0.0316 (5)
O511	−0.2307 (2)	0.27440 (11)	0.78365 (14)	0.0256 (5)
O811	−0.3190 (2)	0.35241 (11)	0.52142 (13)	0.0204 (4)
O812	−0.0757 (2)	0.29573 (12)	0.57293 (14)	0.0271 (5)
O111	0.0408 (2)	0.13710 (12)	0.70094 (13)	0.0230 (4)
O212	−0.3474 (2)	0.13420 (12)	0.65142 (14)	0.0260 (5)
O2	−0.4857 (2)	0.31465 (12)	0.66155 (14)	0.0228 (4)
O412	−0.3727 (2)	0.19907 (11)	0.46253 (13)	0.0215 (4)
O711	0.3056 (2)	0.15899 (12)	0.98797 (15)	0.0308 (5)
O512	0.0052 (2)	0.33892 (11)	0.83143 (13)	0.0214 (4)
O411	0.3855 (2)	0.31657 (12)	0.87600 (15)	0.0317 (5)
C8	−0.0749 (3)	0.42790 (15)	0.51646 (17)	0.0166 (5)
O712	0.0771 (2)	0.18442 (11)	0.89280 (13)	0.0222 (4)
C5	−0.2469 (3)	0.40780 (15)	0.82911 (17)	0.0172 (5)

C81	−0.1595 (3)	0.35232 (15)	0.53885 (18)	0.0177 (5)
C51	−0.1527 (3)	0.33362 (15)	0.81388 (18)	0.0165 (5)
C7	0.0755 (3)	0.07233 (15)	0.98119 (17)	0.0167 (5)
C6	−0.1850 (3)	0.47968 (15)	0.80321 (19)	0.0191 (6)
H6	−0.0866	0.4800	0.7788	0.023*
O5	0.1040 (3)	0.13627 (18)	0.50399 (18)	0.0505 (7)
C4	−0.3963 (3)	0.09269 (15)	0.36547 (17)	0.0159 (5)
O3	−0.1803 (4)	−0.00918 (16)	0.7752 (2)	0.0556 (8)
OW1	−0.4788 (3)	−0.03675 (15)	0.88423 (19)	0.0526 (7)
C2	−0.5855 (3)	0.05086 (15)	0.64934 (18)	0.0161 (5)
C21	−0.4989 (3)	0.12554 (15)	0.62866 (17)	0.0160 (5)
C1	0.2666 (3)	0.05056 (15)	0.68709 (18)	0.0169 (5)
C9	0.1473 (3)	−0.00066 (16)	0.96511 (18)	0.0185 (5)
H9	0.2465	−0.0013	0.9414	0.022*
C11	0.1920 (3)	0.12402 (15)	0.71862 (17)	0.0166 (5)
C3	−0.4787 (3)	0.02144 (16)	0.37516 (18)	0.0194 (6)
H3	−0.5785	0.0219	0.3984	0.023*
C41	−0.4697 (3)	0.16482 (15)	0.40121 (17)	0.0159 (5)
O6	−0.1540 (4)	0.0144 (2)	0.5561 (3)	0.0822 (11)
C71	0.1614 (3)	0.14565 (15)	0.95356 (18)	0.0179 (6)
H42	−0.494 (3)	0.133 (2)	0.824 (2)	0.050*
H22	−0.425 (4)	0.300 (2)	0.7052 (17)	0.050*
H11	0.122 (3)	0.300 (2)	0.6598 (18)	0.050*
H21	−0.481 (4)	0.3594 (12)	0.650 (2)	0.050*
H51	0.088 (5)	0.153 (2)	0.4512 (14)	0.050*
H41	−0.396 (4)	0.136 (2)	0.8981 (15)	0.050*
H52	0.104 (5)	0.0878 (10)	0.499 (2)	0.050*
H31	−0.176 (5)	−0.039 (2)	0.7328 (16)	0.050*
H12	0.282 (2)	0.318 (2)	0.690 (2)	0.050*
H32	−0.166 (5)	−0.0448 (19)	0.8137 (18)	0.050*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01508 (17)	0.01221 (17)	0.0216 (2)	0.00191 (11)	0.00483 (13)	−0.00013 (12)
Cu2	0.01881 (18)	0.01265 (17)	0.0207 (2)	−0.00348 (11)	0.00713 (13)	−0.00177 (13)
Na1	0.0240 (6)	0.0267 (7)	0.0351 (7)	−0.0005 (5)	0.0067 (5)	0.0006 (5)
Na2	0.0270 (6)	0.0356 (7)	0.0363 (8)	0.0007 (5)	0.0054 (5)	0.0006 (6)
O112	0.0192 (9)	0.0127 (9)	0.0264 (11)	0.0019 (7)	0.0021 (8)	−0.0046 (8)
O211	0.0209 (10)	0.0132 (9)	0.0307 (12)	−0.0032 (7)	0.0047 (8)	0.0029 (8)
O1	0.0197 (10)	0.0255 (11)	0.0226 (11)	0.0017 (8)	0.0057 (8)	0.0037 (9)
O4	0.0267 (12)	0.0390 (14)	0.0286 (13)	0.0027 (9)	0.0022 (9)	−0.0038 (10)
O511	0.0274 (11)	0.0149 (10)	0.0328 (13)	0.0023 (8)	−0.0015 (9)	−0.0042 (8)
O811	0.0189 (10)	0.0136 (9)	0.0297 (12)	−0.0050 (7)	0.0063 (8)	0.0008 (8)
O812	0.0270 (11)	0.0190 (11)	0.0338 (13)	−0.0015 (8)	−0.0015 (9)	0.0063 (9)
O111	0.0161 (10)	0.0230 (11)	0.0296 (12)	0.0032 (7)	0.0020 (8)	−0.0030 (8)
O212	0.0175 (10)	0.0261 (11)	0.0338 (13)	−0.0070 (8)	0.0015 (8)	0.0023 (9)
O2	0.0277 (11)	0.0203 (10)	0.0203 (12)	−0.0015 (8)	0.0034 (8)	−0.0017 (9)

O412	0.0198 (9)	0.0197 (10)	0.0255 (11)	−0.0020 (7)	0.0050 (8)	−0.0092 (8)
O711	0.0218 (11)	0.0276 (12)	0.0405 (14)	−0.0103 (8)	−0.0042 (9)	0.0035 (10)
O512	0.0171 (10)	0.0147 (10)	0.0330 (12)	0.0031 (7)	0.0058 (8)	−0.0023 (8)
O411	0.0262 (11)	0.0282 (12)	0.0390 (14)	−0.0121 (9)	−0.0016 (9)	0.0025 (10)
C8	0.0179 (13)	0.0145 (13)	0.0174 (14)	−0.0042 (9)	0.0030 (10)	−0.0013 (10)
O712	0.0223 (10)	0.0199 (10)	0.0246 (11)	−0.0003 (8)	0.0041 (8)	0.0056 (8)
C5	0.0199 (13)	0.0132 (13)	0.0193 (14)	0.0023 (9)	0.0054 (10)	−0.0002 (10)
C81	0.0181 (13)	0.0167 (13)	0.0194 (14)	−0.0027 (10)	0.0064 (10)	−0.0046 (10)
C51	0.0186 (13)	0.0138 (13)	0.0179 (14)	0.0020 (9)	0.0054 (10)	0.0009 (10)
C7	0.0145 (12)	0.0146 (13)	0.0213 (15)	0.0004 (9)	0.0039 (10)	0.0033 (10)
C6	0.0184 (13)	0.0157 (13)	0.0251 (16)	0.0001 (10)	0.0096 (11)	0.0026 (11)
O5	0.0407 (15)	0.075 (2)	0.0365 (16)	−0.0024 (15)	0.0076 (12)	0.0115 (15)
C4	0.0162 (12)	0.0153 (13)	0.0167 (14)	−0.0008 (9)	0.0038 (10)	−0.0028 (10)
O3	0.0532 (16)	0.0305 (15)	0.087 (2)	0.0089 (12)	0.0230 (17)	0.0051 (15)
OW1	0.0622 (17)	0.0350 (15)	0.0592 (19)	−0.0121 (12)	0.0036 (14)	−0.0014 (13)
C2	0.0168 (12)	0.0116 (12)	0.0203 (14)	−0.0009 (9)	0.0045 (10)	0.0001 (10)
C21	0.0177 (13)	0.0132 (12)	0.0188 (14)	−0.0041 (9)	0.0082 (10)	−0.0055 (10)
C1	0.0184 (13)	0.0131 (12)	0.0200 (14)	−0.0001 (9)	0.0049 (10)	−0.0026 (10)
C9	0.0160 (13)	0.0173 (13)	0.0227 (15)	0.0010 (10)	0.0050 (10)	0.0021 (11)
C11	0.0217 (14)	0.0110 (12)	0.0185 (14)	0.0004 (10)	0.0076 (10)	−0.0002 (10)
C3	0.0172 (13)	0.0194 (14)	0.0228 (15)	−0.0013 (10)	0.0074 (11)	−0.0037 (11)
C41	0.0181 (13)	0.0113 (12)	0.0186 (14)	−0.0013 (9)	0.0036 (10)	0.0006 (10)
O6	0.068 (2)	0.073 (2)	0.106 (3)	−0.0037 (17)	0.015 (2)	−0.015 (2)
C71	0.0219 (14)	0.0115 (12)	0.0217 (15)	0.0003 (10)	0.0077 (11)	0.0000 (10)

Geometric parameters (Å, º)

Cu1—O512	1.9450 (17)	O111—C11	1.235 (3)
Cu1—O112	1.9676 (17)	O212—C21	1.235 (3)
Cu1—O712	1.9821 (19)	O412—C41	1.290 (3)
Cu1—O1	2.027 (2)	O711—C71	1.235 (3)
Cu1—O411	2.247 (2)	O711—Cu2ii	2.380 (2)
Cu1—Na1	3.3431 (12)	O512—C51	1.271 (3)
Cu2—O412	1.9523 (18)	O411—C41ii	1.223 (3)
Cu2—O811	1.9519 (17)	C8—C9iii	1.390 (4)
Cu2—O211	1.9603 (18)	C8—C7iv	1.404 (3)
Cu2—O2	2.000 (2)	C8—C81	1.514 (3)
Cu2—O711i	2.380 (2)	O712—C71	1.273 (3)
Cu2—Na2	3.2331 (13)	C5—C6	1.396 (4)
Na1—O4	2.317 (2)	C5—C4v	1.406 (3)
Na1—O111	2.342 (2)	C5—C51	1.504 (3)
Na1—O212	2.384 (2)	C7—C8v	1.404 (3)
Na1—O511	2.396 (2)	C7—C9	1.402 (4)
Na1—O3	2.452 (3)	C7—C71	1.514 (3)
Na1—O712	2.566 (2)	C6—C1iii	1.387 (4)
Na1—Na2	3.5514 (19)	C4—C3	1.396 (4)
Na2—O5	2.266 (3)	C4—C5iv	1.406 (3)
Na2—O6	2.377 (4)	C4—C41	1.499 (3)

Na2—O212	2.379 (2)	C2—C3^{vi}	1.403 (3)
Na2—O111	2.378 (2)	C2—C1^{vii}	1.407 (4)
Na2—O812	2.431 (2)	C2—C21	1.501 (3)
Na2—O412	2.482 (2)	C1—C6^{viii}	1.387 (4)
O112—C11	1.289 (3)	C1—C2^{ix}	1.407 (4)
O211—C21	1.279 (3)	C1—C11	1.495 (3)
O511—C51	1.241 (3)	C9—C8^{viii}	1.390 (4)
O811—C81	1.280 (3)	C3—C2^{vi}	1.403 (3)
O812—C81	1.248 (3)	C41—O411^{i}	1.223 (3)
O512—Cu1—O112	171.78 (8)	O5—Na2—Cu2	140.32 (9)
O512—Cu1—O712	91.64 (8)	O6—Na2—Cu2	120.71 (9)
O112—Cu1—O712	91.24 (8)	O212—Na2—Cu2	57.65 (5)
O512—Cu1—O1	86.91 (8)	O111—Na2—Cu2	120.96 (6)
O112—Cu1—O1	88.24 (8)	O812—Na2—Cu2	65.00 (5)
O712—Cu1—O1	164.40 (8)	O412—Na2—Cu2	37.09 (4)
O512—Cu1—O411	94.25 (8)	O5—Na2—Na1	127.53 (9)
O112—Cu1—O411	92.33 (8)	O6—Na2—Na1	87.46 (10)
O712—Cu1—O411	106.20 (8)	O212—Na2—Na1	41.83 (6)
O1—Cu1—O411	89.40 (8)	O111—Na2—Na1	40.82 (5)
O512—Cu1—Na1	86.34 (6)	O812—Na2—Na1	94.95 (6)
O112—Cu1—Na1	89.62 (6)	O412—Na2—Na1	119.28 (6)
O712—Cu1—Na1	49.99 (6)	Cu2—Na2—Na1	86.65 (3)
O1—Cu1—Na1	114.41 (6)	C11—O112—Cu1	107.64 (15)
O411—Cu1—Na1	156.16 (6)	C21—O211—Cu2	111.63 (16)
O412—Cu2—O811	90.24 (8)	C51—O511—Na1	134.11 (18)
O412—Cu2—O211	91.24 (8)	C81—O811—Cu2	123.53 (17)
O811—Cu2—O211	176.00 (8)	C81—O812—Na2	130.61 (18)
O412—Cu2—O2	160.91 (9)	C11—O111—Na1	131.02 (19)
O811—Cu2—O2	90.52 (8)	C11—O111—Na2	130.92 (18)
O211—Cu2—O2	86.87 (8)	Na1—O111—Na2	97.59 (8)
O412—Cu2—O711^{i}	112.09 (8)	C21—O212—Na2	129.39 (19)
O811—Cu2—O711^{i}	87.53 (8)	C21—O212—Na1	134.18 (18)
O211—Cu2—O711^{i}	95.34 (8)	Na2—O212—Na1	96.43 (8)
O2—Cu2—O711^{i}	86.99 (8)	C41—O412—Cu2	122.04 (16)
O412—Cu2—Na2	50.05 (6)	C41—O412—Na2	133.81 (17)
O811—Cu2—Na2	87.65 (6)	Cu2—O412—Na2	92.86 (8)
O211—Cu2—Na2	90.46 (6)	C71—O711—Cu2^{ii}	157.62 (19)
O2—Cu2—Na2	110.93 (6)	C51—O512—Cu1	123.57 (17)
O711^{i}—Cu2—Na2	161.47 (6)	C41^{ii}—O411—Cu1	162.7 (2)
O4—Na1—O111	167.85 (10)	C9^{iii}—C8—C7^{iv}	119.8 (2)
O4—Na1—O212	87.88 (9)	C9^{iii}—C8—C81	117.9 (2)
O111—Na1—O212	82.84 (8)	C7^{iv}—C8—C81	122.2 (2)
O4—Na1—O511	89.31 (9)	C71—O712—Cu1	128.85 (17)
O111—Na1—O511	97.50 (8)	C71—O712—Na1	127.40 (17)
O212—Na1—O511	84.18 (8)	Cu1—O712—Na1	93.74 (8)
O4—Na1—O3	82.61 (10)	C6—C5—C4^{v}	119.1 (2)
O111—Na1—O3	88.80 (9)	C6—C5—C51	118.0 (2)

O212—Na1—O3	85.32 (11)	C4ᵛ—C5—C51	122.8 (2)
O511—Na1—O3	166.98 (10)	O812—C81—O811	124.2 (2)
O4—Na1—O712	113.41 (9)	O812—C81—C8	120.7 (2)
O111—Na1—O712	77.81 (7)	O811—C81—C8	115.1 (2)
O212—Na1—O712	153.24 (8)	O511—C51—O512	125.5 (2)
O511—Na1—O712	80.26 (7)	O511—C51—C5	119.5 (2)
O3—Na1—O712	112.32 (10)	O512—C51—C5	115.0 (2)
O4—Na1—Cu1	138.94 (8)	C8ᵛ—C7—C9	118.1 (2)
O111—Na1—Cu1	53.08 (5)	C8ᵛ—C7—C71	124.9 (2)
O212—Na1—Cu1	116.99 (6)	C9—C7—C71	116.8 (2)
O511—Na1—Cu1	63.58 (5)	C1ⁱⁱⁱ—C6—C5	121.7 (2)
O3—Na1—Cu1	128.59 (8)	C3—C4—C5ⁱᵛ	119.3 (2)
O712—Na1—Cu1	36.27 (4)	C3—C4—C41	116.2 (2)
O4—Na1—Na2	129.62 (8)	C5ⁱᵛ—C4—C41	124.3 (2)
O111—Na1—Na2	41.59 (6)	C3ᵛⁱ—C2—C1ᵛⁱⁱ	118.8 (2)
O212—Na1—Na2	41.74 (5)	C3ᵛⁱ—C2—C21	118.2 (2)
O511—Na1—Na2	86.20 (7)	C1ᵛⁱⁱ—C2—C21	122.9 (2)
O3—Na1—Na2	91.09 (9)	O212—C21—O211	123.9 (2)
O712—Na1—Na2	115.12 (6)	O212—C21—C2	120.7 (2)
Cu1—Na1—Na2	81.34 (3)	O211—C21—C2	115.3 (2)
O5—Na2—O6	84.46 (12)	C6ᵛⁱⁱⁱ—C1—C2ⁱˣ	119.6 (2)
O5—Na2—O212	161.73 (11)	C6ᵛⁱⁱⁱ—C1—C11	117.5 (2)
O6—Na2—O212	80.49 (11)	C2ⁱˣ—C1—C11	122.8 (2)
O5—Na2—O111	87.09 (9)	C8ᵛⁱⁱⁱ—C9—C7	122.0 (2)
O6—Na2—O111	88.17 (12)	O111—C11—O112	123.0 (2)
O212—Na2—O111	82.16 (8)	O111—C11—C1	120.5 (2)
O5—Na2—O812	89.73 (10)	O112—C11—C1	116.5 (2)
O6—Na2—O812	174.00 (11)	C2ᵛⁱ—C3—C4	121.5 (2)
O212—Na2—O812	104.95 (8)	O411ⁱ—C41—O412	125.4 (2)
O111—Na2—O812	90.07 (8)	O411ⁱ—C41—C4	120.0 (2)
O5—Na2—O412	113.10 (10)	O412—C41—C4	114.4 (2)
O6—Na2—O412	102.21 (11)	O711—C71—O712	127.3 (2)
O212—Na2—O412	80.39 (7)	O711—C71—C7	117.9 (2)
O111—Na2—O412	157.86 (8)	O712—C71—C7	114.7 (2)
O812—Na2—O412	81.41 (7)		

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

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O4—H42···O112ᵛⁱⁱ	0.81 (2)	1.93 (2)	2.737 (3)	174 (4)
O2—H22···O511	0.82 (2)	1.91 (2)	2.697 (3)	162 (4)
O1—H11···O812	0.80 (2)	1.95 (2)	2.708 (3)	159 (4)
O2—H21···O*W*1ˣ	0.78 (2)	1.85 (2)	2.618 (3)	167 (4)
O5—H51···O512ⁱᵛ	0.87 (2)	1.91 (2)	2.744 (3)	161 (4)

O1—H12···O2^{ix}	0.81 (2)	1.99 (2)	2.794 (3)	176 (4)
O3—H32···O1^{viii}	0.85 (2)	2.36 (3)	2.977 (3)	130 (3)

Symmetry codes: (iv) x, $-y+1/2$, $z-1/2$; (vii) $x-1$, y, z; (viii) $-x$, $y-1/2$, $-z+3/2$; (ix) $x+1$, y, z; (x) $-x-1$, $y+1/2$, $-z+3/2$.