Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Hexaaqua(4-chloro-3-formylbenzenesulfonato)calcium(II) 4-chloro-3-formylbenzenesulfonate monohydrate

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Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.004 Å
R factor = 0.035
wR factor = 0.067
Data-to-parameter ratio = 14.3

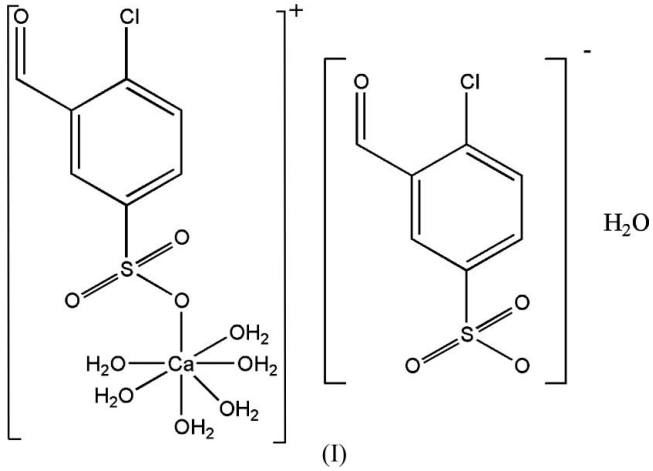
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 16 November 2005
Accepted 12 January 2006

The supramolecular structure of the title molecule, $[Ca(C_7H_4ClO_4S)(H_2O)_6](C_7H_4ClO_4S)\cdot H_2O$, contains alternating organic and inorganic layers along the *b* direction. The sulfonate group on one of the aryl units is coordinated to Ca, while the other does not form any interaction with a Ca atom.

Comment

Previously, the study of supramolecular systems has focused largely on transition metal fragments. However, group II metal salts are also routinely used as building blocks and there has consequently been an increased interest in their structures. Recently, our work (Kennedy *et al.*, 2004) and that of Shimizu & Côté (2003) has focused on the structures of group II metal salts of arylsulfonates. In particular, we have endeavoured to rationalize the nature of the metal–sulfonate bond. This motif is diverse, and is present in many compounds, such as azo colourants, that are of interest to materials chemists.



(I)

The aforementioned work has shown that these species form layered structures with alternate organic and inorganic layers. The magnesium salts of the arylsulfonates typically exist as solvent-separated ion-pairs of the type $[Mg(OH_2)_6][SO_3R]$. As group II is descended, the number and importance of the $M-OSO_2$ bonds increases. The compound reported here, (I), fits well with both of these trends.

The supramolecular structure of (I) contains alternate organic and inorganic layers along the *b* direction. This structure demonstrates the ability of Ca to form $M-OSO_2$ bonds but only in the minimum possible mode of one bond (μ^1,η^1 mode). In this structure, Ca is coordinated by the sulfonate group *via* an O atom and is also solvated by six water molecules, giving it a coordination number of 7. Generally,

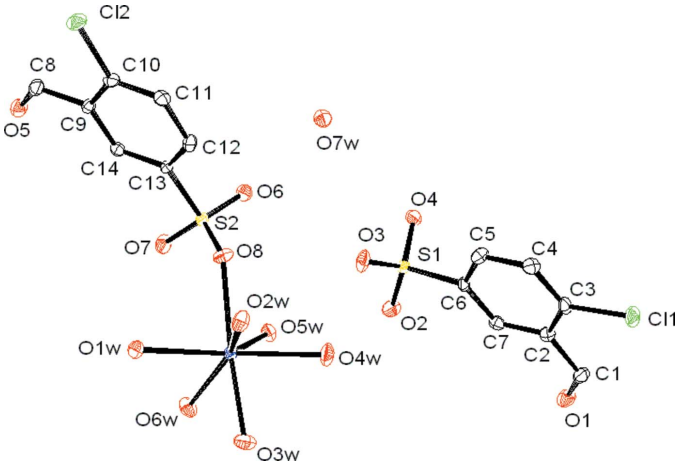


Figure 1
A view of (I), with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Ca—OSO_2 bonds are disfavoured, compared with Sr and Ba, and this is demonstrated well in (I) by the presence of one aryl unit that is not coordinated to Ca. The coordination of the sulfonate O atom to Ca seems to have little effect on the S—O bond length [1.459 (2) Å]. In comparison, the S—O bond lengths of the uncoordinated aryl unit are in the range 1.447–1.462 (2) Å.

Hydrogen bonding (Table 2) is a dominant feature of the crystal structure of (I), with all the H atoms in the water molecules and the sulfonate O atoms being hydrogen bonded. The uncoordinated water molecule acts as both an H-atom donor and acceptor. However, the coordinated water molecules are only donors. π–π stacking in the structure is relatively minor, with the closest distance being 3.353 (4) Å for C2$\cdots$C3^{i} [symmetry code: (i) $x, -y, z+\frac{1}{2}$].

Experimental

Great care was taken during the synthesis. The reaction was carried out within a three-sided Perspex screen in a fume hood and suitable face, eye and body protection was worn. Fuming sulfuric acid (40 ml, 30% SO_3) was cooled in an ice bath, upon which the acid solidified. 2-Chlorobenzaldehyde (5 ml, 44.43 mmol) was added over a period of 2 h, whereupon the acid melted and the solution turned dark brown. Throughout the addition the temperature was maintained below 298 K. The reaction was heated slowly to 358 K and held at that temperature for 45 min. The mixture was kept below 398 K to prevent oxidation of the aldehyde to the carboxylic acid. The solution was then cooled and poured carefully on to ice, after which it was neutralized with calcium carbonate. The mixture was then filtered to remove the resulting calcium sulfate. The filtrate volume was reduced from 600 to 100 ml and the solution was left to stand at room temperature. The product crystallized slowly. Crystals of (I) suitable for X-ray analysis were obtained. These were collected by filtration, washed with diethyl ether and air-dried (yield 72%). Analysis calculated for $C_{14}H_8CaCl_2O_8S_2\cdot 2H_2O$: C 32.62, H 2.35, Cl 13.77, S 12.44%; found: C 32.26, H 1.51, Cl 13.34, S 11.67%; the compound is prone to loss of water, hence the disparity in the H analysis. MS (LC direct): *m/e* 219 $[C_7H_4ClO_4S]^-$.

Crystal data

$[Ca(C_7H_4ClO_4S)(H_2O)_6]$-$(C_7H_4ClO_4S)\cdot H_2O$	D_x = 1.71 Mg m^{-3}
M_r = 605.52	Mo $K\alpha$ radiation
Monoclinic, *Pc*	Cell parameters from 5190 reflections
a = 6.4750 (2) Å	θ = 1.6–27.5°
b = 24.7258 (7) Å	μ = 0.74 mm^{-1}
c = 7.3573 (2) Å	T = 123 (2) K
β = 93.2126 (2)°	Plate, colourless
V = 1176.05 (6) Å^3	0.40 × 0.38 × 0.10 mm
Z = 2	

Data collection

Nonius KappaCCD area-detector diffractometer	4417 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.016
Absorption correction: none	θ_{max} = 27.5°
5205 measured reflections	$h = -8 \rightarrow 8$
5190 independent reflections	$k = -31 \rightarrow 32$
	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0223P)^2 + 0.6115P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.035	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.067	$\Delta\rho_{max}$ = 0.31 e Å^{-3}
S = 1.05	$\Delta\rho_{min}$ = −0.36 e Å^{-3}
5190 reflections	Absolute structure: Flack (1983), with 2483 Friedel pairs
364 parameters	Flack parameter: 0.44 (3)
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Ca1—O3*W*	2.366 (2)	Ca1—O2*W*	2.435 (2)
Ca1—O4*W*	2.367 (2)	Ca1—O5*W*	2.444 (2)
Ca1—O1*W*	2.371 (2)	O1—C1	1.219 (4)
Ca1—O8	2.389 (2)	O5—C8	1.224 (4)
Ca1—O6*W*	2.389 (2)		
O3*W*—Ca1—O4*W*	77.76 (8)	O4*W*—Ca1—O2*W*	77.59 (8)
O3*W*—Ca1—O1*W*	93.04 (8)	O1*W*—Ca1—O2*W*	79.27 (8)
O4*W*—Ca1—O1*W*	156.11 (8)	O8—Ca1—O2*W*	74.11 (7)
O3*W*—Ca1—O8	155.56 (8)	O6*W*—Ca1—O2*W*	150.61 (8)
O4*W*—Ca1—O8	95.37 (8)	O3*W*—Ca1—O5*W*	120.98 (8)
O1*W*—Ca1—O8	83.91 (8)	O4*W*—Ca1—O5*W*	73.89 (8)
O3*W*—Ca1—O6*W*	81.63 (8)	O1*W*—Ca1—O5*W*	128.77 (8)
O4*W*—Ca1—O6*W*	121.67 (9)	O8—Ca1—O5*W*	78.24 (7)
O1*W*—Ca1—O6*W*	77.80 (8)	O6*W*—Ca1—O5*W*	71.59 (7)
O8—Ca1—O6*W*	121.00 (8)	O2*W*—Ca1—O5*W*	137.77 (8)
O3*W*—Ca1—O2*W*	81.49 (8)		

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

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
O1*W*—H1*W*$\cdots$O5^{i}	0.84 (3)	2.08 (3)	2.909 (3)	169 (3)
O1*W*—H2*W*$\cdots$O7*W*^{ii}	0.83 (3)	2.00 (3)	2.806 (3)	161 (4)
O2*W*—H3*W*$\cdots$O4^{iii}	0.83 (3)	1.99 (3)	2.818 (3)	170 (4)
O2*W*—H4*W*$\cdots$O6^{iii}	0.84 (3)	2.07 (3)	2.896 (3)	170 (4)
O3*W*—H5*W*$\cdots$O2^{iii}	0.84 (3)	2.01 (3)	2.842 (3)	172 (4)
O3*W*—H6*W*$\cdots$O4^{ii}	0.83 (3)	1.97 (3)	2.792 (3)	172 (4)
O4*W*—H7*W*$\cdots$O3	0.84 (3)	1.93 (4)	2.739 (3)	164 (5)
O4*W*—H8*W*$\cdots$O1^{iv}	0.83 (3)	2.10 (3)	2.863 (3)	152 (3)
O5*W*—H9*W*$\cdots$O2	0.84 (3)	2.54 (3)	3.296 (3)	151 (3)
O5*W*—H9*W*$\cdots$O3	0.84 (3)	2.54 (3)	3.231 (3)	141 (3)
O5*W*—H10*W*$\cdots$O7*W*^{v}	0.84 (3)	1.95 (3)	2.779 (3)	167 (4)
O6*W*—H11*W*$\cdots$O3^{v}	0.84 (3)	2.08 (3)	2.913 (3)	175 (4)
O6*W*—H12*W*$\cdots$O2*W*^{v}	0.84 (3)	2.34 (3)	3.104 (3)	153 (4)
O6*W*—H12*W*$\cdots$O8^{v}	0.84 (3)	2.49 (3)	3.024 (3)	123 (3)

D—H···A	D—H	H···A	D···A	D—H···A
O7W—H13W···O7^{vi}	0.84 (3)	1.88 (3)	2.703 (3)	168 (3)
O7W—H14W···O6	0.83 (3)	2.01 (3)	2.840 (3)	173 (4)

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

All H atoms were found in a difference Fourier synthesis. Water H atoms were refined isotropically with restraints of O—H = 0.84 (1) and H···H = 1.33 (2) Å. Carbon-bound H atoms were constrained to fit a riding model, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C). The structure was refined as an inversion twin.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); 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, 1999).

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supporting information

Acta Cryst. (2006). E**62**, m339–m341 [https://doi.org/10.1107/S160053680600136X]

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Crystal data

$[Ca(C_7H_4ClO_4S)(H_2O)_6](C_7H_4ClO_4S)\cdot H_2O$
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Monoclinic, *Pc*
$a = 6.4750$ (2) Å
$b = 24.7258$ (7) Å
$c = 7.3573$ (2) Å
$\beta = 93.2126$ (2)°
$V = 1176.05$ (6) Å^3
$Z = 2$
$F(000) = 624$
$D_x = 1.71$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5190 reflections
$\theta = 1.6$–27.5°
$\mu = 0.74$ mm^{-1}
$T = 123$ K
Plate, colourless
0.40 × 0.38 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
5205 measured reflections
5190 independent reflections
4417 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 27.5°$, $\theta_{min} = 1.7°$
$h = -8\rightarrow8$
$k = -31\rightarrow32$
$l = -9\rightarrow9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.067$
$S = 1.05$
5190 reflections
364 parameters
23 restraints
Primary atom site location: structure-invariant direct methods
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
$w = 1/[\sigma^2(F_o^2) + (0.0223P)^2 + 0.6115P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}
Absolute structure: Flack (1983), with how many Friedel pairs
Absolute structure parameter: 0.44 (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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ca1	0.76342 (9)	0.25273 (2)	−0.20523 (8)	0.01176 (12)
Cl1	−0.16585 (12)	−0.04599 (3)	0.02303 (10)	0.02082 (18)
Cl2	0.01852 (11)	0.55155 (3)	−0.14050 (10)	0.02012 (17)
S1	0.36674 (10)	0.15281 (3)	0.29139 (9)	0.01278 (15)
S2	0.56011 (10)	0.35085 (3)	0.09223 (9)	0.01209 (15)
O1	0.4387 (3)	−0.06404 (9)	0.2873 (3)	0.0225 (5)
O2	0.5776 (3)	0.13555 (9)	0.3338 (3)	0.0234 (5)
O1W	0.8627 (4)	0.33185 (9)	−0.3602 (3)	0.0197 (5)
O3	0.3528 (3)	0.19324 (8)	0.1474 (3)	0.0229 (5)
O2W	0.4656 (3)	0.26500 (9)	−0.4183 (3)	0.0191 (5)
O4	0.2627 (3)	0.17060 (8)	0.4522 (3)	0.0192 (5)
O3W	0.8666 (3)	0.19486 (10)	−0.4397 (3)	0.0237 (5)
O5	0.6284 (3)	0.56773 (8)	0.1214 (3)	0.0204 (5)
O4W	0.5664 (4)	0.17392 (9)	−0.1570 (3)	0.0241 (5)
O6	0.4699 (3)	0.33068 (8)	0.2560 (3)	0.0186 (5)
O5W	0.8296 (3)	0.22876 (9)	0.1150 (3)	0.0183 (5)
O7	0.7713 (3)	0.36970 (8)	0.1238 (3)	0.0218 (5)
O6W	1.1283 (3)	0.25531 (10)	−0.1363 (3)	0.0215 (5)
O7W	0.0494 (3)	0.30736 (9)	0.3146 (3)	0.0190 (5)
O8	0.5360 (3)	0.31280 (8)	−0.0591 (3)	0.0188 (5)
C1	0.2698 (5)	−0.05589 (12)	0.2105 (4)	0.0184 (7)
H1	0.1890	−0.0861	0.1698	0.022*
C2	0.1857 (4)	−0.00085 (12)	0.1781 (4)	0.0138 (6)
C3	−0.0081 (4)	0.00810 (12)	0.0907 (4)	0.0156 (6)
C4	−0.0839 (5)	0.06004 (13)	0.0554 (4)	0.0162 (7)
H4	−0.2143	0.0653	−0.0080	0.019*
C5	0.0350 (4)	0.10393 (12)	0.1146 (4)	0.0167 (6)
H5	−0.0146	0.1396	0.0929	0.020*
C6	0.2275 (4)	0.09581 (11)	0.2061 (4)	0.0126 (6)
C7	0.3037 (5)	0.04397 (12)	0.2350 (4)	0.0139 (6)
H7	0.4367	0.0389	0.2937	0.017*
C8	0.4585 (5)	0.56007 (12)	0.0443 (4)	0.0175 (7)
H8	0.3779	0.5906	0.0064	0.021*
C9	0.3727 (4)	0.50526 (11)	0.0074 (4)	0.0127 (6)
C10	0.1751 (4)	0.49700 (12)	−0.0759 (4)	0.0142 (6)
C11	0.0973 (5)	0.44586 (12)	−0.1119 (4)	0.0144 (6)
H11	−0.0362	0.4414	−0.1702	0.017*
C12	0.2172 (4)	0.40104 (12)	−0.0617 (4)	0.0153 (6)
H12	0.1660	0.3656	−0.0855	0.018*
C13	0.4126 (4)	0.40844 (12)	0.0236 (4)	0.0107 (6)
C14	0.4905 (5)	0.45962 (12)	0.0565 (4)	0.0126 (6)
H14	0.6251	0.4639	0.1130	0.015*
H1W	0.785 (4)	0.3587 (9)	−0.377 (4)	0.032 (11)*
H2W	0.937 (5)	0.3305 (16)	−0.449 (4)	0.061 (15)*
H3W	0.392 (6)	0.2392 (11)	−0.455 (5)	0.064 (15)*

H4W	0.481 (7)	0.2854 (13)	−0.507 (4)	0.057 (14)*
H5W	0.777 (4)	0.1763 (13)	−0.497 (4)	0.042 (12)*
H6W	0.979 (3)	0.1871 (16)	−0.482 (5)	0.049 (13)*
H7W	0.505 (7)	0.1733 (18)	−0.060 (4)	0.082 (18)*
H8W	0.530 (5)	0.1456 (9)	−0.211 (4)	0.037 (11)*
H9W	0.737 (4)	0.2152 (13)	0.175 (4)	0.037 (11)*
H10W	0.897 (5)	0.2488 (14)	0.189 (4)	0.049 (13)*
H11W	1.189 (5)	0.2386 (14)	−0.050 (3)	0.044 (12)*
H12W	1.220 (4)	0.2687 (15)	−0.198 (4)	0.049 (13)*
H13W	−0.023 (4)	0.3278 (12)	0.246 (4)	0.031 (10)*
H14W	0.170 (2)	0.3172 (14)	0.298 (5)	0.037 (12)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca1	0.0109 (2)	0.0112 (3)	0.0131 (2)	−0.0004 (2)	−0.0001 (2)	−0.0004 (2)
Cl1	0.0199 (4)	0.0190 (4)	0.0233 (4)	−0.0080 (3)	−0.0011 (3)	−0.0040 (3)
Cl2	0.0200 (4)	0.0176 (4)	0.0226 (4)	0.0073 (3)	−0.0007 (3)	0.0035 (3)
S1	0.0117 (3)	0.0109 (4)	0.0157 (4)	−0.0012 (3)	0.0008 (3)	−0.0013 (3)
S2	0.0114 (3)	0.0101 (3)	0.0146 (3)	0.0006 (3)	−0.0006 (3)	−0.0008 (3)
O1	0.0236 (12)	0.0169 (12)	0.0267 (12)	0.0042 (10)	−0.0013 (10)	0.0024 (10)
O2	0.0106 (10)	0.0211 (12)	0.0376 (13)	−0.0003 (9)	−0.0053 (9)	−0.0100 (10)
O1W	0.0215 (12)	0.0150 (11)	0.0229 (12)	0.0018 (10)	0.0041 (10)	0.0048 (10)
O3	0.0342 (13)	0.0132 (11)	0.0214 (12)	−0.0061 (10)	0.0020 (10)	0.0051 (9)
O2W	0.0226 (12)	0.0152 (12)	0.0187 (11)	−0.0034 (10)	−0.0064 (9)	0.0003 (10)
O4	0.0169 (11)	0.0195 (12)	0.0215 (11)	−0.0048 (9)	0.0054 (9)	−0.0077 (9)
O3W	0.0150 (12)	0.0301 (13)	0.0263 (13)	−0.0014 (11)	0.0041 (10)	−0.0137 (10)
O5	0.0209 (12)	0.0160 (12)	0.0241 (12)	−0.0024 (9)	0.0004 (9)	−0.0021 (9)
O4W	0.0322 (13)	0.0166 (12)	0.0237 (13)	−0.0124 (10)	0.0038 (11)	−0.0027 (10)
O6	0.0201 (11)	0.0175 (11)	0.0183 (11)	0.0020 (9)	0.0016 (9)	0.0054 (9)
O5W	0.0185 (12)	0.0200 (12)	0.0165 (10)	−0.0042 (10)	0.0030 (10)	0.0016 (10)
O7	0.0110 (10)	0.0170 (11)	0.0365 (13)	−0.0024 (9)	−0.0052 (9)	0.0035 (10)
O6W	0.0129 (10)	0.0282 (13)	0.0231 (12)	−0.0008 (10)	−0.0004 (9)	0.0067 (11)
O7W	0.0163 (12)	0.0202 (12)	0.0201 (11)	0.0014 (10)	−0.0014 (10)	0.0031 (9)
O8	0.0211 (11)	0.0162 (11)	0.0190 (11)	0.0053 (9)	0.0000 (9)	−0.0054 (9)
C1	0.0237 (17)	0.0135 (16)	0.0184 (15)	−0.0002 (13)	0.0045 (13)	−0.0022 (13)
C2	0.0157 (14)	0.0154 (15)	0.0101 (13)	−0.0006 (12)	0.0003 (11)	−0.0012 (12)
C3	0.0162 (15)	0.0168 (16)	0.0139 (14)	−0.0076 (12)	0.0028 (12)	−0.0055 (12)
C4	0.0129 (15)	0.0189 (17)	0.0164 (15)	0.0011 (12)	−0.0030 (12)	−0.0024 (12)
C5	0.0193 (16)	0.0129 (15)	0.0176 (15)	0.0030 (13)	−0.0013 (13)	−0.0004 (12)
C6	0.0133 (15)	0.0114 (15)	0.0131 (14)	−0.0047 (12)	0.0016 (12)	−0.0025 (12)
C7	0.0132 (15)	0.0184 (16)	0.0104 (14)	0.0016 (13)	0.0020 (11)	0.0027 (12)
C8	0.0231 (17)	0.0130 (15)	0.0166 (15)	0.0011 (13)	0.0028 (13)	0.0023 (12)
C9	0.0177 (15)	0.0098 (14)	0.0108 (14)	0.0003 (12)	0.0019 (12)	−0.0006 (11)
C10	0.0159 (15)	0.0151 (15)	0.0119 (14)	0.0055 (12)	0.0020 (12)	0.0049 (12)
C11	0.0098 (14)	0.0180 (16)	0.0151 (15)	0.0008 (12)	−0.0017 (11)	0.0015 (12)
C12	0.0173 (15)	0.0122 (15)	0.0163 (14)	−0.0038 (12)	−0.0003 (12)	−0.0013 (12)
C13	0.0113 (13)	0.0090 (14)	0.0119 (13)	−0.0002 (11)	0.0019 (11)	−0.0013 (11)

C14	0.0124 (14)	0.0147 (15)	0.0109 (14)	0.0001 (12)	0.0015 (11)	0.0000 (12)

Geometric parameters (Å, º)

Ca1—O3W	2.366 (2)	O5W—H10W	0.84 (3)
Ca1—O4W	2.367 (2)	O6W—H11W	0.84 (3)
Ca1—O1W	2.371 (2)	O6W—H12W	0.84 (3)
Ca1—O8	2.389 (2)	O7W—H13W	0.84 (3)
Ca1—O6W	2.389 (2)	O7W—H14W	0.83 (3)
Ca1—O2W	2.435 (2)	C1—C2	1.480 (4)
Ca1—O5W	2.444 (2)	C1—H1	0.9500
Cl1—C3	1.739 (3)	C2—C3	1.395 (4)
Cl2—C10	1.738 (3)	C2—C7	1.397 (4)
S1—O2	1.448 (2)	C3—C4	1.394 (4)
S1—O3	1.456 (2)	C4—C5	1.387 (4)
S1—O4	1.462 (2)	C4—H4	0.9500
S1—C6	1.769 (3)	C5—C6	1.397 (4)
S2—O7	1.451 (2)	C5—H5	0.9500
S2—O6	1.456 (2)	C6—C7	1.386 (4)
S2—O8	1.459 (2)	C7—H7	0.9500
S2—C13	1.772 (3)	C8—C9	1.484 (4)
O1—C1	1.219 (4)	C8—H8	0.9500
O1W—H1W	0.84 (3)	C9—C14	1.398 (4)
O1W—H2W	0.83 (3)	C9—C10	1.403 (4)
O2W—H3W	0.83 (3)	C10—C11	1.381 (4)
O2W—H4W	0.84 (3)	C11—C12	1.391 (4)
O3W—H5W	0.84 (3)	C11—H11	0.9500
O3W—H6W	0.83 (3)	C12—C13	1.392 (4)
O5—C8	1.224 (4)	C12—H12	0.9500
O4W—H7W	0.84 (3)	C13—C14	1.379 (4)
O4W—H8W	0.83 (3)	C14—H14	0.9500
O5W—H9W	0.84 (3)		

O3W—Ca1—O4W	77.76 (8)	Ca1—O6W—H11W	125 (2)
O3W—Ca1—O1W	93.04 (8)	Ca1—O6W—H12W	128 (2)
O4W—Ca1—O1W	156.11 (8)	H11W—O6W—H12W	107 (2)
O3W—Ca1—O8	155.56 (8)	H13W—O7W—H14W	103 (2)
O4W—Ca1—O8	95.37 (8)	S2—O8—Ca1	134.59 (12)
O1W—Ca1—O8	83.91 (8)	O1—C1—C2	122.6 (3)
O3W—Ca1—O6W	81.63 (8)	O1—C1—H1	118.7
O4W—Ca1—O6W	121.67 (9)	C2—C1—H1	118.7
O1W—Ca1—O6W	77.80 (8)	C3—C2—C7	118.3 (3)
O8—Ca1—O6W	121.00 (8)	C3—C2—C1	122.2 (3)
O3W—Ca1—O2W	81.49 (8)	C7—C2—C1	119.4 (3)
O4W—Ca1—O2W	77.59 (8)	C4—C3—C2	122.0 (3)
O1W—Ca1—O2W	79.27 (8)	C4—C3—Cl1	117.4 (2)
O8—Ca1—O2W	74.11 (7)	C2—C3—Cl1	120.6 (2)
O6W—Ca1—O2W	150.61 (8)	C5—C4—C3	118.6 (3)

O3W—Ca1—O5W	120.98 (8)	C5—C4—H4	120.7
O4W—Ca1—O5W	73.89 (8)	C3—C4—H4	120.7
O1W—Ca1—O5W	128.77 (8)	C4—C5—C6	120.2 (3)
O8—Ca1—O5W	78.24 (7)	C4—C5—H5	119.9
O6W—Ca1—O5W	71.59 (7)	C6—C5—H5	119.9
O2W—Ca1—O5W	137.77 (8)	C7—C6—C5	120.5 (3)
O2—S1—O3	112.25 (14)	C7—C6—S1	120.8 (2)
O2—S1—O4	112.70 (13)	C5—C6—S1	118.7 (2)
O3—S1—O4	111.70 (13)	C6—C7—C2	120.3 (3)
O2—S1—C6	107.31 (13)	C6—C7—H7	119.9
O3—S1—C6	106.22 (13)	C2—C7—H7	119.9
O4—S1—C6	106.13 (13)	O5—C8—C9	122.9 (3)
O7—S2—O6	113.33 (13)	O5—C8—H8	118.5
O7—S2—O8	112.86 (13)	C9—C8—H8	118.5
O6—S2—O8	112.33 (13)	C14—C9—C10	117.8 (3)
O7—S2—C13	106.00 (13)	C14—C9—C8	119.8 (3)
O6—S2—C13	106.02 (13)	C10—C9—C8	122.4 (3)
O8—S2—C13	105.52 (12)	C11—C10—C9	122.1 (3)
Ca1—O1W—H1W	123 (2)	C11—C10—Cl2	117.2 (2)
Ca1—O1W—H2W	122 (3)	C9—C10—Cl2	120.7 (2)
H1W—O1W—H2W	107 (2)	C10—C11—C12	119.1 (3)
Ca1—O2W—H3W	122 (3)	C10—C11—H11	120.4
Ca1—O2W—H4W	117 (3)	C12—C11—H11	120.4
H3W—O2W—H4W	107 (2)	C11—C12—C13	119.6 (3)
Ca1—O3W—H5W	119 (2)	C11—C12—H12	120.2
Ca1—O3W—H6W	135 (2)	C13—C12—H12	120.2
H5W—O3W—H6W	107 (2)	C14—C13—C12	120.9 (3)
Ca1—O4W—H7W	116 (3)	C14—C13—S2	120.1 (2)
Ca1—O4W—H8W	139 (2)	C12—C13—S2	119.0 (2)
H7W—O4W—H8W	105 (2)	C13—C14—C9	120.4 (3)
Ca1—O5W—H9W	121 (2)	C13—C14—H14	119.8
Ca1—O5W—H10W	123 (3)	C9—C14—H14	119.8
H9W—O5W—H10W	105 (2)		

O7—S2—O8—Ca1	23.9 (2)	C5—C6—C7—C2	−2.1 (4)
O6—S2—O8—Ca1	−105.74 (17)	S1—C6—C7—C2	175.5 (2)
C13—S2—O8—Ca1	139.19 (16)	C3—C2—C7—C6	0.6 (4)
O3W—Ca1—O8—S2	−164.94 (17)	C1—C2—C7—C6	−179.9 (3)
O4W—Ca1—O8—S2	122.98 (17)	O5—C8—C9—C14	−2.0 (4)
O1W—Ca1—O8—S2	−81.02 (17)	O5—C8—C9—C10	177.9 (3)
O6W—Ca1—O8—S2	−9.2 (2)	C14—C9—C10—C11	−0.9 (4)
O2W—Ca1—O8—S2	−161.56 (19)	C8—C9—C10—C11	179.1 (3)
O5W—Ca1—O8—S2	50.70 (17)	C14—C9—C10—Cl2	179.8 (2)
O1—C1—C2—C3	−179.8 (3)	C8—C9—C10—Cl2	−0.1 (4)
O1—C1—C2—C7	0.8 (5)	C9—C10—C11—C12	1.0 (4)
C7—C2—C3—C4	1.5 (4)	Cl2—C10—C11—C12	−179.7 (2)
C1—C2—C3—C4	−177.9 (3)	C10—C11—C12—C13	0.0 (4)
C7—C2—C3—Cl1	−178.0 (2)	C11—C12—C13—C14	−1.0 (4)

C1—C2—C3—Cl1	2.6 (4)	C11—C12—C13—S2	178.3 (2)
C2—C3—C4—C5	−2.1 (4)	O7—S2—C13—C14	−17.5 (3)
Cl1—C3—C4—C5	177.4 (2)	O6—S2—C13—C14	103.2 (2)
C3—C4—C5—C6	0.6 (4)	O8—S2—C13—C14	−137.4 (2)
C4—C5—C6—C7	1.5 (4)	O7—S2—C13—C12	163.2 (2)
C4—C5—C6—S1	−176.2 (2)	O6—S2—C13—C12	−76.1 (2)
O2—S1—C6—C7	17.5 (3)	O8—S2—C13—C12	43.3 (3)
O3—S1—C6—C7	137.8 (2)	C12—C13—C14—C9	1.1 (4)
O4—S1—C6—C7	−103.2 (3)	S2—C13—C14—C9	−178.2 (2)
O2—S1—C6—C5	−164.8 (2)	C10—C9—C14—C13	−0.1 (4)
O3—S1—C6—C5	−44.5 (3)	C8—C9—C14—C13	179.8 (3)
O4—S1—C6—C5	74.5 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···O5^{i}	0.84 (3)	2.08 (3)	2.909 (3)	169 (3)
O1*W*—H2*W*···O7*W*^{ii}	0.83 (3)	2.00 (3)	2.806 (3)	161 (4)
O2*W*—H3*W*···O4^{iii}	0.83 (3)	1.99 (3)	2.818 (3)	170 (4)
O2*W*—H4*W*···O6^{iii}	0.84 (3)	2.07 (3)	2.896 (3)	170 (4)
O3*W*—H5*W*···O2^{iii}	0.84 (3)	2.01 (3)	2.842 (3)	172 (4)
O3*W*—H6*W*···O4^{ii}	0.83 (3)	1.97 (3)	2.792 (3)	172 (4)
O4*W*—H7*W*···O3	0.84 (3)	1.93 (4)	2.739 (3)	164 (5)
O4*W*—H8*W*···O1^{iv}	0.83 (3)	2.10 (3)	2.863 (3)	152 (3)
O5*W*—H9*W*···O2	0.84 (3)	2.54 (3)	3.296 (3)	151 (3)
O5*W*—H9*W*···O3	0.84 (3)	2.54 (3)	3.231 (3)	141 (3)
O5*W*—H10*W*···O7*W*^{v}	0.84 (3)	1.95 (3)	2.779 (3)	167 (4)
O6*W*—H11*W*···O3^{v}	0.84 (3)	2.08 (3)	2.913 (3)	175 (4)
O6*W*—H12*W*···O2*W*^{v}	0.84 (3)	2.34 (3)	3.104 (3)	153 (4)
O6*W*—H12*W*···O8^{v}	0.84 (3)	2.49 (3)	3.024 (3)	123 (3)
O7*W*—H13*W*···O7^{vi}	0.84 (3)	1.88 (3)	2.703 (3)	168 (3)
O7*W*—H14*W*···O6	0.83 (3)	2.01 (3)	2.840 (3)	173 (4)

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