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

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Key indicators

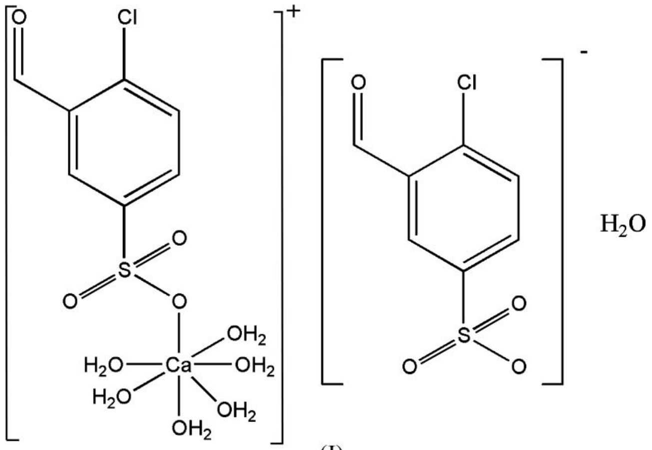
Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.004 Å
R factor = 0.035
wR factor = 0.067
Data-to-parameter ratio = 14.3

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

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,

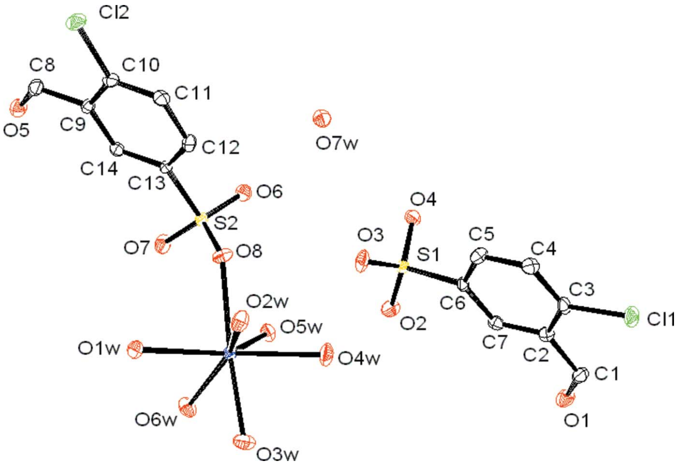


Figure 1
A view of (I), with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

$Ca-OSO_2$ 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

$[Ca(C_7H_4ClO_4S)(H_2O)_6]$-
$(C_7H_4ClO_4S)\cdot H_2O$
$M_r = 605.52$
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
$Z = 2$

$D_x = 1.71$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5190 reflections
$\theta = 1.6$–27.5°
$\mu = 0.74$ mm^{-1}
$T = 123$ (2) K
Plate, colourless
0.40 × 0.38 × 0.10 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: none
5205 measured reflections
5190 independent reflections

4417 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\rm max} = 27.5°$
$h = -8 \rightarrow 8$
$k = -31 \rightarrow 32$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.067$
$S = 1.05$
5190 reflections
364 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0223P)^2 + 0.6115P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.31$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.36$ e Å^{-3}
Absolute structure: Flack (1983), with 2483 Friedel pairs
Flack parameter: 0.44 (3)

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, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1W-H1W\cdots O5^{i}$	0.84 (3)	2.08 (3)	2.909 (3)	169 (3)
$O1W-H2W\cdots O7W^{ii}$	0.83 (3)	2.00 (3)	2.806 (3)	161 (4)
$O2W-H3W\cdots O4^{iii}$	0.83 (3)	1.99 (3)	2.818 (3)	170 (4)
$O2W-H4W\cdots O6^{iii}$	0.84 (3)	2.07 (3)	2.896 (3)	170 (4)
$O3W-H5W\cdots O2^{iii}$	0.84 (3)	2.01 (3)	2.842 (3)	172 (4)
$O3W-H6W\cdots O4^{ii}$	0.83 (3)	1.97 (3)	2.792 (3)	172 (4)
$O4W-H7W\cdots O3$	0.84 (3)	1.93 (4)	2.739 (3)	164 (5)
$O4W-H8W\cdots O1^{iv}$	0.83 (3)	2.10 (3)	2.863 (3)	152 (3)
$O5W-H9W\cdots O2$	0.84 (3)	2.54 (3)	3.296 (3)	151 (3)
$O5W-H9W\cdots O3$	0.84 (3)	2.54 (3)	3.231 (3)	141 (3)
$O5W-H10W\cdots O7W^{v}$	0.84 (3)	1.95 (3)	2.779 (3)	167 (4)
$O6W-H11W\cdots O3^{v}$	0.84 (3)	2.08 (3)	2.913 (3)	175 (4)
$O6W-H12W\cdots O2W^{v}$	0.84 (3)	2.34 (3)	3.104 (3)	153 (4)
$O6W-H12W\cdots O8^{v}$	0.84 (3)	2.49 (3)	3.024 (3)	123 (3)

m340 Wallace *et al.* • $[Ca(C_7H_4ClO_4S)(H_2O)_6](C_7H_4ClO_4S)\cdot H_2O$ *Acta Cryst.* (2006). E**62**, m339–m341

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
$O7W—H13W\cdots O7^{vi}$	0.84 (3)	1.88 (3)	2.703 (3)	168 (3)
$O7W—H14W\cdots O6$	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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Acta Cryst. (2006). E**62**, m339–m341 Wallace *et al.* • $[Ca(C_7H_4ClO_4S)(H_2O)_6](C_7H_4ClO_4S)\cdot H_2O$ **m341**