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Crystal engineering with short-chained amphiphiles: decasodium octa-*n*-butanesulfonate di-μ-chlorido-bis[dichloridopalladate(II)] tetrahydrate, a layered inorganic–organic hybrid material

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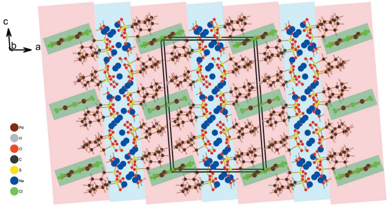
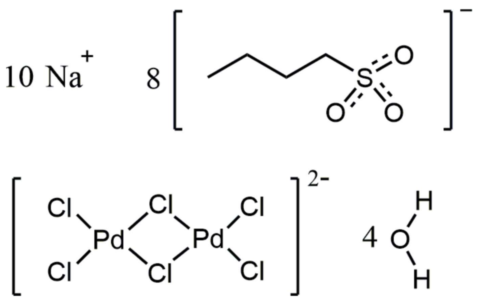
In the course of crystal-engineering experiments, crystals of the hydrated title salt, $Na_{10}[Pd_2Cl_6](C_4H_9SO_3)_8 \cdot 4H_2O$, were obtained from a water/2-propanol solution of sodium *n*-butanesulfonate and sodium tetrachloridopalladate(II). In the crystal, sodium *n*-butanesulfonate anions and water molecules are arranged in an amphiphilic inverse bilayered cationic array represented by the formula $\{[Na_{10}(C_4H_9SO_3)_8(H_2O)_4]^{2+}\}_n$. Within this lamellar array: (i) a hydrophilic layer region parallel to the *bc* plane is established by the Na^+ cations, the H_2O molecules (as aqua ligands in $\kappa Na,\kappa Na'$-bridging coordination mode) and the O_3S– groups of the sulfonate ions, and (ii) hydrophobic regions are present containing all the *n*-butyl groups in an almost parallel orientation, with the chain direction approximately perpendicular to the aforementioned hydrophilic layer. Unexpectedly, the flat centrosymmetric $[Pd_2Cl_6]^{2-}$ anion in the structure is placed between the butyl groups, *within* the hydrophobic regions, but due to its appropriate length primarily bonded to the hydrophilic 'inorganic' layer regions above and below the hydrophobic area *via* $Pd—Cl_t\cdots Na$- and $Pd—Cl_t\cdots H—O(H)—Na$-type (Cl_t is terminal chloride) interactions. In addition to these hydrogen-bonding interactions, both aqua ligands are engaged in charge-supported $S—O\cdots H—O$ hydrogen bonds of a motif characterized by the $D_4^3(9)$ graph-set descriptor within the hydrophilic region. The crystal structure of the title compound is the first reported for a metal *n*-butanesulfonate.

1. Chemical context

Sodium alkanesulfonates are artificial soaps (anionic tensides) with a widespread use (Schramm *et al.*, 2003). They are known to have a bilayered structure like 'natural' soaps, with an extreme tendency for disorder in the crystalline state (Buerger, 1942; Buerger *et al.*, 1942). Compounds containing alkanesulfonate ions of the general formula $C_nH_{2n+1}SO_3^-$ with $n = 1–4$ may be defined as short-chained alkanesulfonates (SCAS). In contrast to methanesulfonates ($n = 1$) and ethanesulfonates ($n = 2$), there is only rare structure information for the next higher homologues ($n = 3, 4$) (Frank & Jablonka, 2008; Russell *et al.*, 1994). Solid sodium methanesulfonate is described as an inorganic–organic three-dimensional network (Wei & Hingerty, 1981). However, closer inspection shows the compound to have a bilayered soap-like structure with only one of five $CH_3SO_3^-$ anions connecting in the third dimension. In crystal-engineering experiments, we successfully exchanged this connecting anion by selected other ionic moieties and were able to retain the lamellar structure (Thoelen & Frank, 2017, 2018; Verheyen & Frank, 2009). An



aim of subsequent attempts was to include chloridopalladate(II) anions $Pd_nCl_{2n+2}^{2-}$ that are known to be catalytically active (Bouquillion *et al.*, 1999; Jimeno *et al.*, 2012; Lassahn *et al.*, 2003; Mu *et al.*, 2012), by using $[PdCl_4]^{2-}$ in the form of its sodium salt as a typical precursor in aqueous palladium(II) chemistry.



In the investigation described herein, the incorporation of hexachloridodipalladate(II) anions into the sodium *n*-butanesulfonate layered system was realized, resulting in the title compound (**1**) having the typical brown colour of palladium complexes with a square-planar coordination environment. According to the results of elemental analysis and vibrational spectroscopic investigations, hydrated sodium cations, *n*-butanesulfonate and hexachloridodipalladate(II) anions are present in the solid. The crystal structure determination of this compound is the first of a metal *n*-butanesulfonate and eventually confirmed the composition $Na_{10}(C_4H_9SO_3)_8[Pd_2Cl_6]\cdot 4H_2O$ and a lamellar amphiphilic structure.

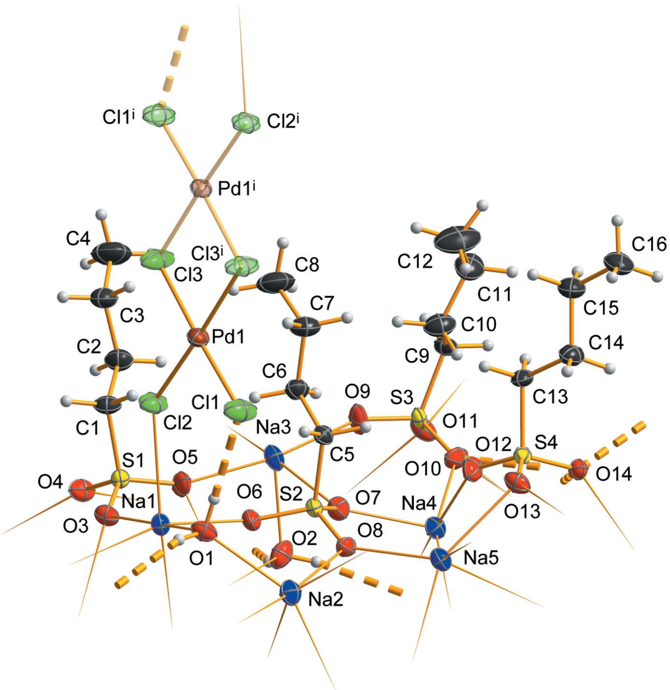


Figure 1
The asymmetric unit of **1**, chosen to give a compact segment with all *n*-butyl groups of the hydrophobic layer region oriented in one direction. In addition, the symmetry-related second half of the hexachlorido-dipallate(II) anion is shown in transparent mode [symmetry code: (i) $-x, 1-y, 1-z$.]. The direction of coordinative bonding to atoms of neighbouring moieties is given by sharpened sticks, and hydrogen bonds are shown as segmented solid bonds. Displacement ellipsoids are drawn at the 50% probability level, hydrogen atoms are drawn with an arbitrary radius. Note the coordination of the hexachloridodipalladate(II) ion to hydrophilic moieties by hydrogen bonding and 'local' ionic interactions.

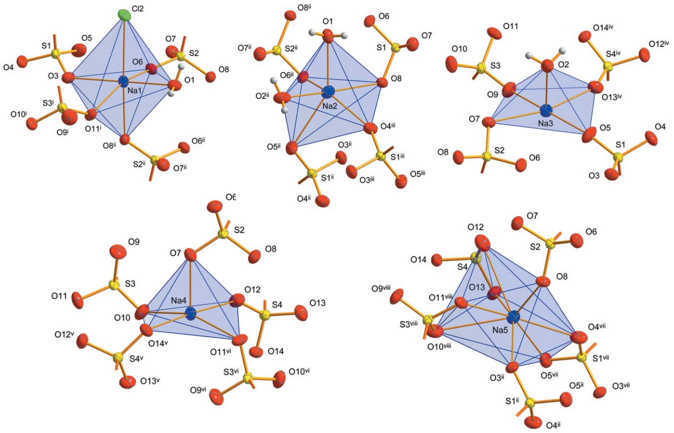


Figure 2
Coordination environments of sodium cations. For clarity, *n*-butylgroups of the *n*-butanesulfonate anions are not shown. [Symmetry codes: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $1-x, 1-y, 1-z$; (iii) $x, 1+y, z$; (iv) $x, -1+y, z$; (v) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (vi) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$]. The Na—O distances [Na1—O = 2.284 (3)–2.540 (3) Å; Na2—O = 2.283 (3)–2.700 (3) Å; Na3—O = 2.212 (2)–2.649 (3) Å; Na4—O = 2.308 (5)–2.479 (3) Å; Na5—O = 2.391 (3)–3.000 (4) Å] are within the reported range for short-chained sodium alkanesulfonates (Wei & Hingerty, 1981).

2. Structural commentary

Fig. 1 shows the asymmetric unit of the crystal structure that contains (all in general positions) five sodium cations, two water molecules, four *n*-butanesulfonate anions and, close to a center of inversion, one half of a hexachloridodipalladate anion. The five Na^+ cations are in quite different coordination environments (Fig. 2), defined by five sulfonato ligands (Na4, Na5), four sulfonato ligands and one aqua ligand (Na3), four sulfonato ligands and two aqua ligands (Na2) and four sulfonato ligands, one aqua ligand and one terminal chlorido ligand of the $[Pd_2Cl_6]^{2-}$ anion (Na1). Bond lengths and angles of the *n*-butanesulfonate anions are as expected (see supplementary Tables). All these anions are found with an entirely *anti*-periplanar conformation of the alkyl groups, without any disorder. Altogether, *n*-butanesulfonate anions, Na^+ cations and water molecules form a tenside-like inverse bilayered cationic array, which can be described by the formula $\{[Na_{10}(H_2O)_4(C_4H_9SO_3)_8]^{2+}\}_n$. In this arrangement, the layer-like regions are oriented parallel to the *bc* plane of the unit cell. As visualized by the blue and the red sections of the transparent background of Fig. 3, hydrophilic and hydrophobic regions are given, reminiscent of sections of the structures of 'pure' short-chained sodium alkanesulfonates (Frank & Jablonka, 2008; Wei & Hingerty, 1981). The hydrophilic areas contain the Na^+ cations, the H_2O molecules serving as aqua ligands in $\mu(\kappa Na,\kappa Na')$ bridging mode coordination, and the O_3S– groups of the sulfonate ions. With all the C_4-chains in an approximately parallel orientation, the butyl groups are arranged on both sides of the hydrophilic region to complete the amphiphilic double layer with an inverse bilayer thickness according to unit-cell parameter *a*. The centrosymmetric $[Pd_2Cl_6]^{2-}$ anions in the structure of **1** are placed between the *n*-butyl groups *within the hydrophobic regions*. In a first view, this position seems to be unexpected; however, the length of the dipalladate(II) anion is appropriate to allow for pronounced bonding to the hydrophilic 'inorganic' layered regions above and below the hydrophobic area (Fig. 3). To interact with the inorganic areas above and below the hydrophobic region, a building block is needed that fits to the thickness of the hydrophobic double layer. In the concrete case of **1**, the thickness is determined by the lengths of two 'end-facing' *n*-butyl groups.

As expected, the Pd—Cl bonds to the terminal chlorido ligands [2.2776 (12) and 2.2800 (10) Å] are slightly shorter than the Pd—μ-Cl bonds [2.3159 (11) and 2.3212 (12) Å]. These geometric parameters, as well as the Cl—Pd—Cl bond angles of 86.20 (4) to 92.45 (4)° and the Pd—μ-Cl—Pd angle of 93.80 (4)°, are in good agreement with those found in $Cs_2[Pd_2Cl_6]$ (Schüpp & Keller, 1999) or in several hexachloridodipalladates with large organic cations (*e.g.* Chitanda *et al.*, 2008; Gerisch *et al.*, 1997; Makitova *et al.*, 2007). Alternatively to the formula given above, compound **1** might be formulated as a hydrated double salt of sodium *n*-butanesulfonate and sodium hexachloridodipalladate(II): $Na_8(C_4H_9SO_3)_8 \cdot Na_2Pd_2Cl_6 \cdot 4H_2O$. This choice takes into account that the Na—Cl distance from the terminal chlorido ligand Cl2 of the hexachloridodipalladate(II) anion to the sodium cation Na1 [2.8560 (18) Å] is close to the distances of 2.809 (3) to 2.821 (2) Å in Na_2PdCl_4 (Schröder & Keller, 1989). However, this is a singular similarity, and because all the sodium cations of **1** clearly are components of the layer-like hydrophilic region, there is a much closer structural relationship of **1** to sodium methanesulfonate (Wei & Hingerty, 1981) and sodium 1-propanesulfonate monohydrate (Frank & Jablonka, 2008). As in the structures of these compounds, the asymmetric unit in **1** contains five Na^+ cations, establishing a closely related Na—O coordination network, and the separation of hydrophilic layers and hydrophobic areas is similar to the most prominent structural feature of crystallized amphiphiles where the neighbouring hydrophobic areas in the layer-like structures are connected by van der Waals forces only.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O14^{i}	0.80 (3)	2.10 (4)	2.879 (4)	164 (5)
O1—H2$\cdots$Cl1	0.82 (3)	2.32 (4)	3.127 (3)	172 (6)
O2—H3$\cdots$O10^{ii}	0.81 (3)	1.95 (4)	2.723 (4)	159 (5)
O2—H4$\cdots$O14^{ii}	0.80 (3)	2.10 (4)	2.884 (4)	164 (6)

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

3. Supramolecular features

As emphasized in Fig.1, in addition to the coordinative bonding to two Na^+ cations [O1—Na1 = 2.326 (3) Å, O1—Na2 = 2.407 (4) Å; O2—Na3 = 2.311 (4) Å, O2—Na2′ = 2.488 (4) Å], the two crystallographically independent water molecules O1 and O2 in **1** are engaged in non-covalent bonding within the hydrophilic region (Table 1). The water

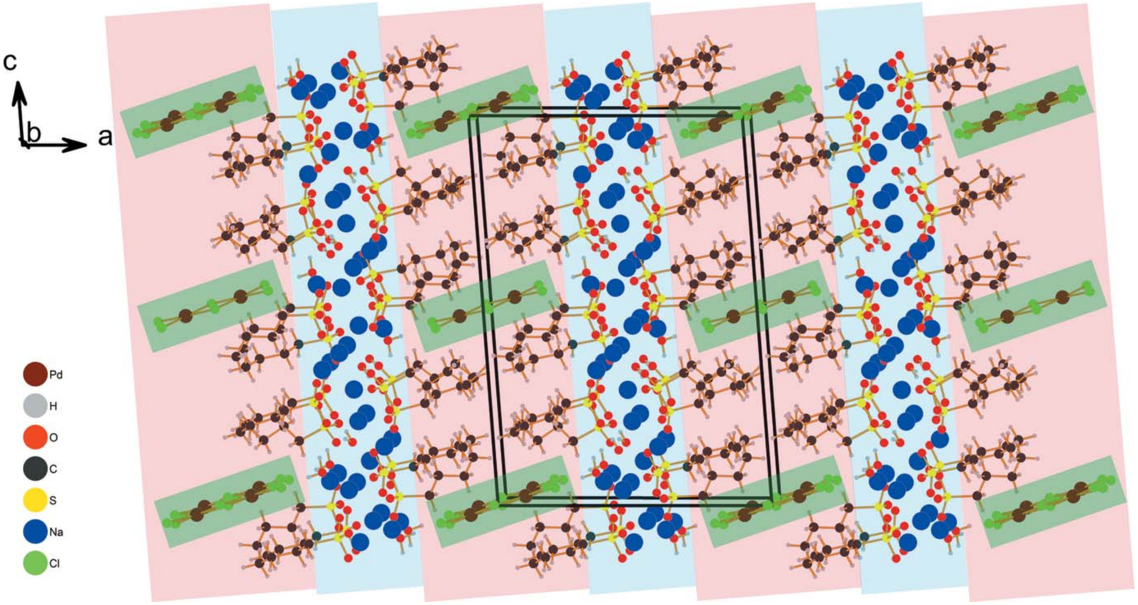


Figure 3
Diagram displaying hydrophilic (blue) and hydrophobic sections (red) of the bilayered amphiphile packing of **1**; layers are parallel to the *bc* plane of the unit cell. Note the inverse bilayer thickness corresponding to the unit-cell dimension along [100]. The hexachloridodipalladate(II) anions are placed within the hydrophobic region but are primarily bonded to the hydrophilic.

Table 2
Experimental details.

Crystal data	
Chemical formula	$Na_{10}[Pd_2Cl_6](C_4H_9O_3S)_8 \cdot 4H_2O$
M_r	1824.84
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	213
a, b, c (Å)	15.9049 (4), 9.9047 (2), 22.6734 (7)
β (°)	94.315 (2)
V (Å^3)	3561.69 (16)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.10
Crystal size (mm)	0.43 × 0.13 × 0.06
Data collection	
Diffractometer	Stoe IPDS_2T
Absorption correction	Multi-scan (*PLATON*; Spek, 2009)
T_{min}, T_{max}	0.650, 0.937
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	48866, 8183, 7116
R_{int}	0.072
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.062, 0.099, 1.54
No. of reflections	8183
No. of parameters	408
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.73, −0.43

Computer programs: *X-AREA* (Stoe & Cie, 2009), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg, 2016) and *publCIF* (Westrip, 2010).

molecule containing O1 serves as donor for both a charge-supported O—H⋯Cl-type hydrogen bond of medium strength to one of the terminal chlorido ligands of the $[Pd_2Cl_6]^{2-}$ anion [$D \cdots A$ distance = 3.127 (3) Å] and a charge-supported weak O—H⋯O type hydrogen bond to an O atom of a sulfonate anion containing S4 [$D \cdots A$ = 2.879 (4) Å]. In contrast, the water molecule containing O2 is engaged in two O—H⋯O type hydrogen bonds to sulfonate ions, one of moderate strength to an O atom of the sulfonate ion containing S4 [$D \cdots A$ = 2.723 (4) Å] and a weak one to an O atom of the sulfonate ion containing S3 [$D \cdots A$ = 2.884 (4) Å]. $Pd-Cl_{term} \cdots H-O(Na_2)-H \cdots O14(S4) \cdots H-O(Na_2)-H \cdots O-S$ is the entire path of hydrogen bonding described by the $D_4^3(9)$ graph-set descriptor (Russell *et al.*, 1994; Grell *et al.*, 1999), with the sulfonate oxygen atom O14 as the central double acceptor.

4. Database survey

A search in the Cambridge Structural Database (Version 5.40, update November 2018; Groom *et al.*, 2016) for short-chained sodium alkanesulfonates $Na(C_nH_{2n+1}SO_3)$ with n = 1–4 gave three hits, *viz.* the structures of sodium methanesulfonate (BAKLAA; Wei & Hingerty, 1981), sodium 1-propanesulfonate monohydrate (GOKHIY; Frank & Jablonka, 2008) and α-cyclodextrin sodium 1-propanesulfonate nonahydrate (ACDPRS; Harata, 1977). For crystal structures with *n*-butanesulfonate anions, only one entry was found (WETNUE; Russell *et al.*, 1994), describing the lamellar structure of guanidinium *n*-butanesulfonate. Searching for the hexachloridodipalladate(II) anion results in 46 entries. However, from a structural point of view, the role of the $[Pd_2Cl_6]^{2-}$ ion in **1** is completely different from the role of this species in all the other compounds. In addition to the reports on these compounds having organic components, there is one report on an inorganic ternary chloride containing the $[Pd_2Cl_6]^{2-}$ ion ($CsPdCl_3$; Schüpp & Keller, 1999).

5. Synthesis and Crystallization

Thin brown platelets of **1** were obtained by slow isothermal evaporation of the solvent from a solution of 5 ml of distilled water and 5 ml of isopropanol containing 3.203 g (20 mmol) of sodium *n*-butanesulfonate and 1.177 g (4 mmol) of sodium tetrachloridopalladate(II). The evaporation temperature of the solution was adjusted to 288 K with a thermostat. After three days, crystals suitable for X-ray crystal structure determination could be harvested (5.985 g; 81.6% based on $PdCl_4^{2-}$). A single crystal was selected directly from the mother liquor. Raman spectroscopy was done with a Bruker MultiRAM spectrometer, equipped with a Nd:YAG laser (1064 nm) and an InGaAs detector (4000–70 cm^{-1}): ν(C—H): 2969 (*m*), 2920 (*s*), 2872 (*m*); δ_s(C—H): 1445 (*w*), 1412 (*w*); δ_{as}(C—H): 1306 (*w*); ν_{as}(S—O): 1071 (*s*); ν_s(C—S): 800 (*m*); δ(S—O): 551 (*m*), 536 (*m*); ν(Pd—Cl$_{term}$): 343 (*m*), ν(Pd—μ-Cl): 305 (*s*); ν(Pd—μ-Cl): 273 (*m*). Band assignments were made according to Fujimori (1959) and Gerisch *et al.* (1997). An IR spectrum was recorded by using a Spektrum Two FT–IR spectrometer (Perkin Elmer company) with an $LiTaO_3$ detector (4000–350 cm^{-1}) and an universal ATR equipment: ν(O—H): 3503 (*s*), 3462 (*sh*), 3436 (*s*), 3367 (s); ν(C—H): 2967 (*s*), 2936 (*s*), 2872 (*m*); δ(O—H): 1662 (*m*), 1602 (*m*); δ_s(C—H) 1465 (*m*), 1412 (*w*), 1378 (*w*), δ_{as}(C—H): 1314 (*w*), 1286 (*w*); ν_{as}(C—H): 1241 (*w*); ν_s(S—O): 1190 (*s*), 1166 (s); ν_{as}(S—O): 1057 (*s*), 1044 (*s*); ν_s(C—S): 794 (*m*); δ(S—O): 555 (*m*), 534 (*m*); band assignment according to Fujimori (1959). A CHS analysis was performed with a vario micro cube (Elementar Analysensysteme GmbH). Analysis calculated for $C_{32}H_{80}Cl_6Na_{10}O_{28}Pd_2S_8$ (1824.84 g mol^{-1}): C 21.06, H 4.42, S 14.06; found: C 20.78, H 4.49, S 12.98.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The positions of all hydrogen atoms were identified in difference-Fourier syntheses. In the course of the converging refinement, a riding model was applied using idealized C—H bond lengths (0.97–0.98 Å) as well as H—C—H and C—C—H angles. In addition, H atoms of CH_3 groups were allowed to rotate around the neighboring C—C bonds. The U_{iso}(H) values were set to $1.5U_{eq}(C_{methyl})$ and $1.2U_{eq}(C_{methylene})$, respectively. H—O distances of the water molecules were restrained to 0.83 (3) Å.

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supporting information

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Crystal engineering with short-chained amphiphiles: decasodium octa-*n*-butanesulfonate di-*μ*-chlorido-bis[dichloridopalladate(II)] tetrahydrate, a layered inorganic–organic hybrid material

Felix Thoelen and Walter Frank

Computing details

Data collection: *X-AREA* (Stoe & Cie, 2009); cell refinement: *X-AREA* (Stoe & Cie, 2009); data reduction: *X-AREA* (Stoe & Cie, 2009); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 2016); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Decasodium octa-*n*-butanesulfonate di-*μ*-chlorido-bis[dichloridopalladate(II)] tetrahydrate

Crystal data

$Na_{10}[Pd_2Cl_6](C_4H_9O_3S)_8\cdot4H_2O$
M_r = 1824.84
Monoclinic, $P2_1/c$
a = 15.9049 (4) Å
b = 9.9047 (2) Å
c = 22.6734 (7) Å
β = 94.315 (2)°
V = 3561.69 (16) Å^3
Z = 2
$F(000)$ = 1856
D_x = 1.702 Mg m^{-3}
D_m = 1.712 Mg m^{-3}
D_m measured by flotation in chloroform/bromoform
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 49957 reflections
θ = 4.1–59.3°
μ = 1.10 mm^{-1}
T = 213 K
Thin platelets, brown
0.43 × 0.13 × 0.06 mm

Data collection

Stoe IPDS_2T diffractometer
ω scan
Absorption correction: multi-scan (*PLATON*; Spek, 2009)
T_{min} = 0.650, T_{max} = 0.937
48866 measured reflections
8183 independent reflections
7116 reflections with $I > 2\sigma(I)$
R_{int} = 0.072
θ_{max} = 27.5°, θ_{min} = 2.1°
$h = -20\rightarrow20$
$k = -11\rightarrow12$
$l = -29\rightarrow29$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.099
S = 1.54
8183 reflections
408 parameters
4 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0215P)^2 + 3.8152P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.73$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ 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.

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

	x	y	z	U_{iso}*/U_{eq}
Pd1	0.10273 (2)	0.51478 (3)	0.52464 (2)	0.02493 (8)
Cl1	0.18814 (7)	0.69241 (11)	0.55153 (7)	0.0452 (3)
Cl2	0.20910 (6)	0.36261 (11)	0.54280 (6)	0.0361 (3)
Cl3	0.01032 (7)	0.34122 (11)	0.49624 (7)	0.0465 (3)
S1	0.37572 (5)	0.04330 (8)	0.48827 (4)	0.01605 (17)
S2	0.40803 (5)	0.51616 (8)	0.41684 (4)	0.01565 (17)
S3	0.37879 (6)	0.32626 (9)	0.19446 (4)	0.01684 (17)
S4	0.35920 (5)	0.87006 (9)	0.26546 (4)	0.01710 (17)
Na1	0.38885 (9)	0.35553 (15)	0.55924 (7)	0.0216 (3)
Na2	0.46690 (10)	0.73138 (16)	0.54410 (7)	0.0283 (4)
Na3	0.38987 (10)	0.20007 (16)	0.34308 (7)	0.0274 (3)
Na4	0.48859 (9)	0.56786 (15)	0.28553 (7)	0.0230 (3)
Na5	0.46642 (10)	0.86689 (15)	0.39298 (7)	0.0245 (3)
O1	0.36894 (19)	0.5796 (3)	0.58556 (14)	0.0283 (6)
H1	0.367 (3)	0.583 (5)	0.6209 (15)	0.037 (15)*
H2	0.322 (2)	0.604 (6)	0.574 (3)	0.054 (18)*
O2	0.5354 (2)	0.1883 (3)	0.35206 (15)	0.0329 (7)
H3	0.556 (3)	0.116 (4)	0.344 (2)	0.040 (15)*
H4	0.552 (4)	0.240 (5)	0.328 (2)	0.053 (18)*
O3	0.40321 (17)	0.1195 (3)	0.54127 (12)	0.0241 (6)
O4	0.40499 (17)	−0.0958 (3)	0.49020 (14)	0.0291 (6)
O5	0.40033 (19)	0.1094 (3)	0.43503 (13)	0.0334 (7)
O6	0.41514 (16)	0.4210 (3)	0.46581 (12)	0.0250 (6)
O7	0.43673 (17)	0.4534 (3)	0.36366 (12)	0.0248 (6)
O8	0.45103 (16)	0.6439 (3)	0.43105 (12)	0.0232 (6)
O9	0.3628 (2)	0.2671 (3)	0.25054 (13)	0.0351 (7)
O10	0.42717 (18)	0.4508 (3)	0.20055 (14)	0.0317 (7)
O11	0.41987 (17)	0.2306 (3)	0.15672 (12)	0.0268 (6)
O12	0.38437 (18)	0.7351 (3)	0.28429 (14)	0.0318 (7)
O13	0.37292 (17)	0.9671 (3)	0.31322 (12)	0.0282 (6)
O14	0.39915 (16)	0.9112 (3)	0.21230 (11)	0.0227 (6)
C1	0.2645 (2)	0.0366 (4)	0.48516 (18)	0.0263 (8)
H1A	0.247524	−0.006022	0.521426	0.032*
H1B	0.242490	0.129115	0.484160	0.032*
C2	0.2242 (3)	−0.0399 (5)	0.4324 (2)	0.0322 (9)
H2A	0.237766	0.005670	0.395932	0.039*

H2B	0.247891	−0.131170	0.431978	0.039*
C3	0.1293 (3)	−0.0491 (5)	0.4338 (2)	0.0397 (11)
H3A	0.115781	−0.088804	0.471540	0.048*
H3B	0.105327	0.042000	0.431444	0.048*
C4	0.0894 (4)	−0.1334 (8)	0.3836 (3)	0.0677 (19)
H4A	0.101675	−0.093553	0.346175	0.102*
H4B	0.028870	−0.136552	0.386313	0.102*
H4C	0.112114	−0.224331	0.386268	0.102*
C5	0.2997 (2)	0.5537 (4)	0.40159 (18)	0.0218 (8)
H5A	0.276788	0.588722	0.437482	0.026*
H5B	0.293682	0.624250	0.371248	0.026*
C6	0.2495 (2)	0.4298 (4)	0.3802 (2)	0.0280 (9)
H6A	0.272963	0.394351	0.344612	0.034*
H6B	0.255302	0.359666	0.410749	0.034*
C7	0.1563 (3)	0.4605 (5)	0.3663 (2)	0.0372 (10)
H7A	0.149960	0.526981	0.334304	0.045*
H7B	0.133087	0.499702	0.401316	0.045*
C8	0.1075 (3)	0.3334 (6)	0.3481 (3)	0.0614 (17)
H8A	0.048969	0.356374	0.337654	0.092*
H8B	0.110742	0.269793	0.380703	0.092*
H8C	0.131600	0.292931	0.314234	0.092*
C9	0.2808 (2)	0.3675 (4)	0.15778 (17)	0.0248 (8)
H9A	0.290621	0.413088	0.120555	0.030*
H9B	0.250007	0.283805	0.147917	0.030*
C10	0.2260 (3)	0.4574 (5)	0.1931 (2)	0.0374 (11)
H10A	0.210258	0.408265	0.228162	0.045*
H10B	0.258374	0.537204	0.206608	0.045*
C11	0.1472 (3)	0.5017 (6)	0.1572 (3)	0.0472 (13)
H11A	0.119599	0.421943	0.138975	0.057*
H11B	0.163221	0.560869	0.125302	0.057*
C12	0.0847 (3)	0.5754 (6)	0.1927 (4)	0.070 (2)
H12A	0.040022	0.612826	0.166142	0.105*
H12B	0.113199	0.647803	0.215028	0.105*
H12C	0.060712	0.512844	0.219803	0.105*
C13	0.2498 (2)	0.8633 (4)	0.2452 (2)	0.0265 (8)
H13A	0.239772	0.797174	0.213276	0.032*
H13B	0.220841	0.831048	0.279147	0.032*
C14	0.2112 (2)	0.9972 (4)	0.2249 (2)	0.0315 (9)
H14A	0.242041	1.032898	0.192421	0.038*
H14B	0.217053	1.062014	0.257575	0.038*
C15	0.1180 (3)	0.9829 (5)	0.2040 (2)	0.0379 (10)
H15A	0.112726	0.920407	0.170397	0.045*
H15B	0.087968	0.943249	0.235982	0.045*
C16	0.0765 (3)	1.1155 (5)	0.1856 (2)	0.0432 (12)
H16A	0.106069	1.155756	0.154136	0.065*
H16B	0.078677	1.176286	0.219272	0.065*
H16C	0.018177	1.099456	0.171769	0.065*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pd1	0.01842 (13)	0.02374 (15)	0.03245 (17)	0.00385 (12)	0.00072 (11)	0.00322 (13)
Cl1	0.0311 (5)	0.0272 (5)	0.0747 (9)	0.0030 (4)	−0.0117 (5)	−0.0018 (6)
Cl2	0.0231 (5)	0.0286 (5)	0.0551 (7)	0.0068 (4)	−0.0055 (5)	0.0019 (5)
Cl3	0.0225 (5)	0.0257 (5)	0.0895 (10)	0.0045 (4)	−0.0078 (6)	0.0017 (6)
S1	0.0189 (4)	0.0142 (4)	0.0150 (4)	−0.0004 (3)	0.0011 (3)	−0.0014 (3)
S2	0.0176 (4)	0.0146 (4)	0.0147 (4)	0.0009 (3)	0.0008 (3)	0.0012 (3)
S3	0.0225 (4)	0.0154 (4)	0.0123 (4)	−0.0003 (3)	−0.0002 (3)	0.0009 (3)
S4	0.0165 (4)	0.0174 (4)	0.0174 (4)	0.0015 (3)	0.0016 (3)	0.0020 (3)
Na1	0.0265 (8)	0.0197 (7)	0.0185 (7)	0.0001 (6)	0.0012 (6)	0.0020 (6)
Na2	0.0318 (8)	0.0238 (8)	0.0295 (9)	0.0042 (7)	0.0027 (7)	0.0019 (7)
Na3	0.0344 (9)	0.0290 (8)	0.0187 (8)	0.0055 (7)	0.0024 (6)	0.0036 (7)
Na4	0.0250 (7)	0.0195 (7)	0.0245 (8)	0.0035 (6)	0.0015 (6)	−0.0007 (6)
Na5	0.0280 (8)	0.0232 (7)	0.0219 (8)	0.0031 (6)	−0.0008 (6)	0.0017 (6)
O1	0.0271 (15)	0.0317 (16)	0.0252 (16)	0.0021 (13)	−0.0040 (13)	−0.0052 (13)
O2	0.0381 (17)	0.0225 (15)	0.0397 (19)	−0.0021 (13)	0.0135 (14)	−0.0004 (14)
O3	0.0264 (14)	0.0263 (14)	0.0193 (13)	0.0004 (11)	−0.0005 (11)	−0.0071 (11)
O4	0.0261 (14)	0.0174 (13)	0.0431 (18)	0.0043 (11)	−0.0029 (13)	−0.0030 (12)
O5	0.0380 (16)	0.0452 (18)	0.0170 (14)	−0.0123 (14)	0.0007 (12)	0.0077 (13)
O6	0.0236 (13)	0.0268 (14)	0.0242 (15)	0.0010 (11)	−0.0007 (11)	0.0086 (12)
O7	0.0265 (14)	0.0274 (14)	0.0209 (14)	0.0038 (11)	0.0048 (11)	−0.0024 (11)
O8	0.0241 (13)	0.0175 (12)	0.0273 (15)	−0.0027 (10)	−0.0028 (11)	0.0005 (11)
O9	0.0493 (19)	0.0403 (17)	0.0161 (14)	−0.0015 (15)	0.0045 (13)	0.0069 (13)
O10	0.0278 (15)	0.0198 (13)	0.0465 (19)	−0.0052 (12)	−0.0046 (13)	0.0022 (13)
O11	0.0306 (15)	0.0288 (14)	0.0205 (14)	0.0124 (12)	−0.0017 (11)	−0.0062 (12)
O12	0.0288 (15)	0.0237 (14)	0.0432 (19)	0.0058 (12)	0.0055 (13)	0.0122 (13)
O13	0.0287 (14)	0.0345 (16)	0.0207 (14)	0.0046 (12)	−0.0021 (11)	−0.0062 (12)
O14	0.0222 (13)	0.0282 (14)	0.0177 (13)	−0.0032 (11)	0.0024 (10)	0.0017 (11)
C1	0.0175 (17)	0.031 (2)	0.030 (2)	0.0028 (15)	0.0008 (15)	−0.0085 (17)
C2	0.030 (2)	0.035 (2)	0.032 (2)	−0.0031 (18)	−0.0025 (17)	−0.0074 (19)
C3	0.023 (2)	0.044 (3)	0.050 (3)	−0.0036 (19)	−0.0059 (19)	0.005 (2)
C4	0.040 (3)	0.091 (5)	0.069 (4)	−0.017 (3)	−0.016 (3)	−0.008 (4)
C5	0.0198 (17)	0.0196 (17)	0.026 (2)	0.0039 (14)	0.0010 (15)	0.0023 (15)
C6	0.025 (2)	0.0258 (19)	0.032 (2)	−0.0028 (16)	−0.0032 (16)	−0.0009 (17)
C7	0.0211 (19)	0.044 (3)	0.046 (3)	−0.0001 (19)	−0.0029 (18)	−0.004 (2)
C8	0.031 (3)	0.065 (4)	0.086 (5)	−0.014 (3)	−0.012 (3)	−0.004 (3)
C9	0.0201 (18)	0.034 (2)	0.0195 (19)	0.0016 (16)	−0.0022 (14)	−0.0025 (17)
C10	0.027 (2)	0.036 (2)	0.050 (3)	0.0024 (18)	0.0039 (19)	−0.010 (2)
C11	0.033 (2)	0.046 (3)	0.062 (3)	0.013 (2)	0.007 (2)	0.010 (3)
C12	0.032 (3)	0.058 (4)	0.120 (6)	0.013 (3)	0.005 (3)	−0.020 (4)
C13	0.0148 (17)	0.029 (2)	0.036 (2)	−0.0021 (15)	0.0011 (15)	0.0046 (18)
C14	0.0227 (19)	0.028 (2)	0.043 (3)	0.0036 (16)	−0.0029 (17)	0.0034 (19)
C15	0.023 (2)	0.045 (3)	0.045 (3)	0.0004 (19)	−0.0025 (18)	0.007 (2)
C16	0.027 (2)	0.051 (3)	0.051 (3)	0.010 (2)	−0.003 (2)	0.009 (2)

Geometric parameters (Å, º)

Pd1—Cl1	2.2776 (12)	O1—H2	0.82 (3)
Pd1—Cl2	2.2800 (10)	O2—H3	0.81 (3)
Pd1—Cl3^{i}	2.3159 (11)	O2—H4	0.80 (3)
Pd1—Cl3	2.3212 (12)	C1—C2	1.517 (6)
Cl2—Na1	2.8560 (18)	C1—H1A	0.9800
S1—O5	1.453 (3)	C1—H1B	0.9800
S1—O4	1.453 (3)	C2—C3	1.514 (6)
S1—O3	1.458 (3)	C2—H2A	0.9800
S1—C1	1.767 (4)	C2—H2B	0.9800
S2—O6	1.454 (3)	C3—C4	1.512 (8)
S2—O7	1.460 (3)	C3—H3A	0.9800
S2—O8	1.462 (3)	C3—H3B	0.9800
S2—C5	1.771 (4)	C4—H4A	0.9700
S3—O9	1.440 (3)	C4—H4B	0.9700
S3—O10	1.455 (3)	C4—H4C	0.9700
S3—O11	1.463 (3)	C5—C6	1.524 (5)
S3—C9	1.759 (4)	C5—H5A	0.9800
S4—O12	1.451 (3)	C5—H5B	0.9800
S4—O13	1.452 (3)	C6—C7	1.522 (6)
S4—O14	1.462 (3)	C6—H6A	0.9800
S4—C13	1.767 (4)	C6—H6B	0.9800
Na1—O6	2.284 (3)	C7—C8	1.520 (7)
Na1—O1	2.326 (3)	C7—H7A	0.9800
Na1—O11^{ii}	2.386 (3)	C7—H7B	0.9800
Na1—O3	2.387 (3)	C8—H8A	0.9700
Na1—O8^{iii}	2.540 (3)	C8—H8B	0.9700
Na2—O4^{iv}	2.283 (3)	C8—H8C	0.9700
Na2—O1	2.407 (4)	C9—C10	1.516 (6)
Na2—O6^{iii}	2.431 (3)	C9—H9A	0.9800
Na2—O2^{iii}	2.488 (4)	C9—H9B	0.9800
Na2—O5^{iii}	2.649 (3)	C10—C11	1.507 (7)
Na2—O8	2.700 (3)	C10—H10A	0.9800
Na3—O9	2.212 (3)	C10—H10B	0.9800
Na3—O5	2.264 (3)	C11—C12	1.514 (7)
Na3—O2	2.311 (4)	C11—H11A	0.9800
Na3—O13^{v}	2.414 (3)	C11—H11B	0.9800
Na3—O7	2.649 (3)	C12—H12A	0.9700
Na4—O7	2.308 (3)	C12—H12B	0.9700
Na4—O12	2.342 (3)	C12—H12C	0.9700
Na4—O14^{vi}	2.363 (3)	C13—C14	1.519 (6)
Na4—O10	2.393 (3)	C13—H13A	0.9800
Na4—O11^{vii}	2.479 (3)	C13—H13B	0.9800
Na5—O8	2.391 (3)	C14—C15	1.529 (6)
Na5—O13	2.462 (3)	C14—H14A	0.9800
Na5—O3^{iii}	2.465 (3)	C14—H14B	0.9800
Na5—O4^{iv}	2.505 (3)	C15—C16	1.515 (6)

Na5—O11^{vii}	2.582 (3)	C15—H15A	0.9800
Na5—O5^{iv}	2.817 (4)	C15—H15B	0.9800
Na5—O10^{vii}	2.931 (4)	C16—H16A	0.9700
Na5—O12	3.000 (4)	C16—H16B	0.9700
O1—H1	0.80 (3)	C16—H16C	0.9700

Cl1—Pd1—Cl2	92.45 (4)	O5^{iv}—Na5—O12	119.93 (10)
Cl1—Pd1—Cl3^{i}	90.99 (4)	O10^{vii}—Na5—O12	76.60 (9)
Cl2—Pd1—Cl3^{i}	176.53 (4)	Na1—O1—H1	108 (4)
Cl1—Pd1—Cl3	177.19 (4)	Na2—O1—H1	116 (4)
Cl2—Pd1—Cl3	90.36 (4)	Na1—O1—H2	109 (4)
Cl3^{i}—Pd1—Cl3	86.20 (4)	Na2—O1—H2	107 (4)
Pd1—Cl2—Na1	139.61 (5)	H1—O1—H2	102 (5)
Pd1^{i}—Cl3—Pd1	93.80 (4)	Na3—O2—Na2^{iii}	88.93 (12)
O5—S1—O4	110.28 (19)	Na3—O2—H3	116 (4)
O5—S1—O3	111.62 (17)	Na2^{iii}—O2—H3	122 (4)
O4—S1—O3	112.98 (17)	Na3—O2—H4	107 (4)
O5—S1—C1	108.38 (19)	Na2^{iii}—O2—H4	117 (4)
O4—S1—C1	106.46 (18)	H3—O2—H4	104 (5)
O3—S1—C1	106.83 (17)	C2—C1—S1	114.3 (3)
O5—S1—Na5^{v}	61.48 (14)	C2—C1—H1A	108.7
O6—S2—O7	110.06 (17)	S1—C1—H1A	108.7
O6—S2—O8	112.61 (17)	C2—C1—H1B	108.7
O7—S2—O8	112.35 (16)	S1—C1—H1B	108.7
O6—S2—C5	107.70 (17)	H1A—C1—H1B	107.6
O7—S2—C5	106.74 (17)	C3—C2—C1	112.1 (4)
O8—S2—C5	107.05 (17)	C3—C2—H2A	109.2
O9—S3—O10	112.86 (19)	C1—C2—H2A	109.2
O9—S3—O11	111.67 (18)	C3—C2—H2B	109.2
O10—S3—O11	110.37 (18)	C1—C2—H2B	109.2
O9—S3—C9	107.65 (19)	H2A—C2—H2B	107.9
O10—S3—C9	106.94 (19)	C4—C3—C2	112.3 (4)
O11—S3—C9	107.02 (18)	C4—C3—H3A	109.1
O12—S4—O13	111.59 (18)	C2—C3—H3A	109.1
O12—S4—O14	111.84 (17)	C4—C3—H3B	109.1
O13—S4—O14	112.33 (17)	C2—C3—H3B	109.1
O12—S4—C13	106.62 (18)	H3A—C3—H3B	107.9
O13—S4—C13	107.99 (19)	C3—C4—H4A	109.5
O14—S4—C13	106.06 (18)	C3—C4—H4B	109.5
O6—Na1—O1	90.30 (12)	H4A—C4—H4B	109.5
O6—Na1—O11^{ii}	157.10 (12)	C3—C4—H4C	109.5
O1—Na1—O11^{ii}	97.25 (12)	H4A—C4—H4C	109.5
O6—Na1—O3	95.34 (11)	H4B—C4—H4C	109.5
O1—Na1—O3	174.22 (12)	C6—C5—S2	111.9 (3)
O11^{ii}—Na1—O3	78.00 (10)	C6—C5—H5A	109.2
O6—Na1—O8^{iii}	80.06 (10)	S2—C5—H5A	109.2
O1—Na1—O8^{iii}	97.50 (11)	C6—C5—H5B	109.2
O11^{ii}—Na1—O8^{iii}	77.54 (10)	S2—C5—H5B	109.2

O3—Na1—O8^{iii}	84.77 (10)	H5A—C5—H5B	107.9
O6—Na1—Cl2	97.08 (9)	C7—C6—C5	112.6 (3)
O1—Na1—Cl2	81.71 (9)	C7—C6—H6A	109.1
O11^{ii}—Na1—Cl2	105.37 (9)	C5—C6—H6A	109.1
O3—Na1—Cl2	96.29 (8)	C7—C6—H6B	109.1
O8^{iii}—Na1—Cl2	177.04 (9)	C5—C6—H6B	109.1
O4^{iv}—Na2—O1	114.31 (12)	H6A—C6—H6B	107.8
O4^{iv}—Na2—O6^{iii}	136.11 (12)	C6—C7—C8	111.1 (4)
O1—Na2—O6^{iii}	100.08 (11)	C6—C7—H7A	109.4
O4^{iv}—Na2—O2^{iii}	103.31 (12)	C8—C7—H7A	109.4
O1—Na2—O2^{iii}	76.94 (11)	C6—C7—H7B	109.4
O6^{iii}—Na2—O2^{iii}	110.63 (12)	C8—C7—H7B	109.4
O4^{iv}—Na2—O5^{iii}	87.44 (11)	H7A—C7—H7B	108.0
O1—Na2—O5^{iii}	146.38 (12)	C7—C8—H8A	109.5
O6^{iii}—Na2—O5^{iii}	77.03 (11)	C7—C8—H8B	109.5
O2^{iii}—Na2—O5^{iii}	73.07 (11)	H8A—C8—H8B	109.5
O4^{iv}—Na2—O8	74.15 (10)	C7—C8—H8C	109.5
O1—Na2—O8	98.82 (11)	H8A—C8—H8C	109.5
O6^{iii}—Na2—O8	74.38 (10)	H8B—C8—H8C	109.5
O2^{iii}—Na2—O8	173.81 (12)	C10—C9—S3	114.2 (3)
O5^{iii}—Na2—O8	112.15 (10)	C10—C9—H9A	108.7
O9—Na3—O5	171.09 (14)	S3—C9—H9A	108.7
O9—Na3—O2	102.75 (13)	C10—C9—H9B	108.7
O5—Na3—O2	83.98 (13)	S3—C9—H9B	108.7
O9—Na3—O13^{v}	90.64 (12)	H9A—C9—H9B	107.6
O5—Na3—O13^{v}	83.01 (12)	C11—C10—C9	111.9 (4)
O2—Na3—O13^{v}	93.81 (12)	C11—C10—H10A	109.2
O9—Na3—O7	85.12 (11)	C9—C10—H10A	109.2
O5—Na3—O7	102.30 (12)	C11—C10—H10B	109.2
O2—Na3—O7	76.45 (11)	C9—C10—H10B	109.2
O13^{v}—Na3—O7	168.18 (11)	H10A—C10—H10B	107.9
O7—Na4—O12	93.62 (11)	C10—C11—C12	114.0 (5)
O7—Na4—O14^{vi}	88.54 (10)	C10—C11—H11A	108.8
O12—Na4—O14^{vi}	176.01 (12)	C12—C11—H11A	108.8
O7—Na4—O10	103.43 (11)	C10—C11—H11B	108.8
O12—Na4—O10	95.00 (12)	C12—C11—H11B	108.8
O14^{vi}—Na4—O10	87.75 (11)	H11A—C11—H11B	107.7
O7—Na4—O11^{vii}	98.26 (11)	C11—C12—H12A	109.5
O12—Na4—O11^{vii}	86.19 (12)	C11—C12—H12B	109.5
O14^{vi}—Na4—O11^{vii}	90.18 (11)	H12A—C12—H12B	109.5
O10—Na4—O11^{vii}	158.15 (12)	C11—C12—H12C	109.5
O8—Na5—O13	124.40 (12)	H12A—C12—H12C	109.5
O8—Na5—O3^{iii}	86.35 (10)	H12B—C12—H12C	109.5
O13—Na5—O3^{iii}	148.92 (12)	C14—C13—S4	114.4 (3)
O8—Na5—O4^{iv}	76.20 (10)	C14—C13—H13A	108.7
O13—Na5—O4^{iv}	109.44 (11)	S4—C13—H13A	108.7
O3^{iii}—Na5—O4^{iv}	79.97 (10)	C14—C13—H13B	108.7
O8—Na5—O11^{vii}	76.62 (10)	S4—C13—H13B	108.7

O13—Na5—O11$^{\text{vii}}$	107.11 (10)	H13A—C13—H13B	107.6
O3$^{\text{iii}}$—Na5—O11$^{\text{vii}}$	72.99 (9)	C13—C14—C15	111.9 (4)
O4$^{\text{iv}}$—Na5—O11$^{\text{vii}}$	142.52 (11)	C13—C14—H14A	109.2
O8—Na5—O5$^{\text{iv}}$	127.94 (10)	C15—C14—H14A	109.2
O13—Na5—O5$^{\text{iv}}$	71.62 (10)	C13—C14—H14B	109.2
O3$^{\text{iii}}$—Na5—O5$^{\text{iv}}$	93.85 (10)	C15—C14—H14B	109.2
O4$^{\text{iv}}$—Na5—O5$^{\text{iv}}$	52.85 (9)	H14A—C14—H14B	107.9
O11$^{\text{vii}}$—Na5—O5$^{\text{iv}}$	152.22 (10)	C16—C15—C14	113.4 (4)
O8—Na5—O10$^{\text{vii}}$	127.13 (10)	C16—C15—H15A	108.9
O13—Na5—O10$^{\text{vii}}$	72.78 (9)	C14—C15—H15A	108.9
O3$^{\text{iii}}$—Na5—O10$^{\text{vii}}$	85.23 (10)	C16—C15—H15B	108.9
O4$^{\text{iv}}$—Na5—O10$^{\text{vii}}$	151.57 (11)	C14—C15—H15B	108.9
O11$^{\text{vii}}$—Na5—O10$^{\text{vii}}$	51.04 (8)	H15A—C15—H15B	107.7
O5$^{\text{iv}}$—Na5—O10$^{\text{vii}}$	104.68 (9)	C15—C16—H16A	109.5
O8—Na5—O12	81.05 (10)	C15—C16—H16B	109.5
O13—Na5—O12	51.00 (9)	H16A—C16—H16B	109.5
O3$^{\text{iii}}$—Na5—O12	144.57 (10)	C15—C16—H16C	109.5
O4$^{\text{iv}}$—Na5—O12	127.80 (10)	H16A—C16—H16C	109.5
O11$^{\text{vii}}$—Na5—O12	71.92 (9)	H16B—C16—H16C	109.5

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O14$^{\text{viii}}$	0.80 (3)	2.10 (4)	2.879 (4)	164 (5)
O1—H2···Cl1	0.82 (3)	2.32 (4)	3.127 (3)	172 (6)
O2—H3···O10$^{\text{vi}}$	0.81 (3)	1.95 (4)	2.723 (4)	159 (5)
O2—H4···O14$^{\text{vi}}$	0.80 (3)	2.10 (4)	2.884 (4)	164 (6)

Symmetry codes: (vi) −*x*+1, *y*−1/2, −*z*+1/2; (viii) *x*, −*y*+3/2, *z*+1/2.