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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1055). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Sodium 1,12-Dodecylene Disulfate Hydrate

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Abstract

There are two independent dodecylene disulfate molecules in the crystal of $2\text{Na}^+ \cdot \text{C}_{12}\text{H}_{24}\text{O}_8\text{S}_2^{2-} \cdot 2/3\text{H}_2\text{O}$, one with a centrosymmetric conformation, its center lying on a crystallographic center of symmetry, the second with an asymmetric conformation, which is partially disordered. The molecules form a layer structure parallel to the *ab* plane, the polar parts of neighbouring molecular layers connecting *via* coordination to the Na^+ ion. Additionally, there are hydrogen bonds between the water molecule and two sulfate groups.

Comment

The crystal structures of sodium dodecyl sulfate hydrate with varying water content have been reported by sev-

eral authors (Sundell, 1977; Coiro, Mazza & Pochetti, 1986; Coiro, Manigrasso, Mazza & Pochetti, 1987). The role of head groups in the structural arrangement can be demonstrated by a comparison of the crystal structures of sodium dodecyl sulfate and sodium dodecylene disulfate. The interactions within the layer planes as a function of the number of sulfate groups of both amphiphilic compounds are of interest with respect to the characterization of adsorption layers at the interfaces. This is the first example of a crystal structure determination of sodium 1,12-dodecylene disulfate hydrate, (I).

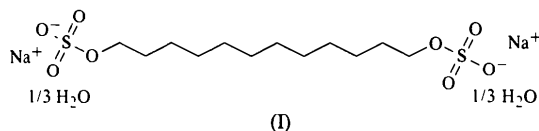


Fig. 1 shows the asymmetric unit together with the atomic numbering scheme. One disulfate molecule is centrosymmetric with the center of the molecule situated at a crystallographic inversion center. The second molecule, which has an asymmetric conformation, is in a general position and has disorder of every second C atom (*i.e.* atoms with numbers ending in 2, 4, 6...12) of its hydrocarbon chain and of three O atoms of a sulfate group. The apparently short C—C distances and the wide C—C—C angles of this molecule are probably artefacts caused by the difficulties refining pairs of disordered atoms.

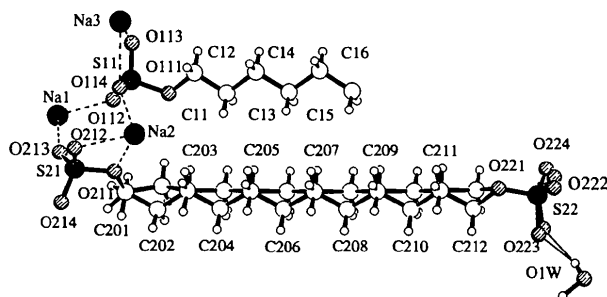


Fig. 1. Drawing of the asymmetric unit. Shaded circles are O atoms, filled circles are S atoms and Na^+ cations, dotted lines are $\text{Na}^+ \cdots \text{O}$ contacts, and thin lines are hydrogen bridges. For the disordered pairs only the labels of one atom are shown.

The hydrocarbon chain in both molecules is planar with the exception of C201 of the disordered molecule. C201 deviates from the least squares plane by 0.102 (5) Å (plane defined by the atoms C201–C212, first-chain orientation) and by 0.257 (5) Å (plane defined by C201, C302, C203–C312, second-chain orientation). The torsion angles O—C—C—C are antiperiplanar for both the ordered molecule and for the C212/C312 side of the disordered molecule and synclinal on the C201 side of the same molecule (this holds for both parts of the disordered pair). This kind of torsion angle is normally antiperiplanar in dodecyl sulfates, but there is

an example of a synclinal conformation in the literature (Coiro, Manigrasso, Mazza & Pochetti, 1987).

The S—O(ester) bond lengths are significantly longer than the other S—O bond lengths of the sulfate groups. This has also been observed in other crystal structures of alkyl sulfates.

The molecules form layers which are connected to each other by Na⁺·O coordination (Fig. 2). The area per head group in each layer is 23.23 (3) Å². This supports the hypothesis that the area per head group in sodium alkyl sulfates is linearly dependent on the water content and can be estimated by the equation $A = 20.56 + 9.35x$ Å², where x is the number of water molecules per head group (Rudert, Vollhardt & Czichocki, 1996); $x = 1/3$ in the title structure. The distances of the S atoms to the $z = 0$ plane are between 0.7353 (6) and 3.2720 (6) Å, thus allowing favourable electrostatic interactions.

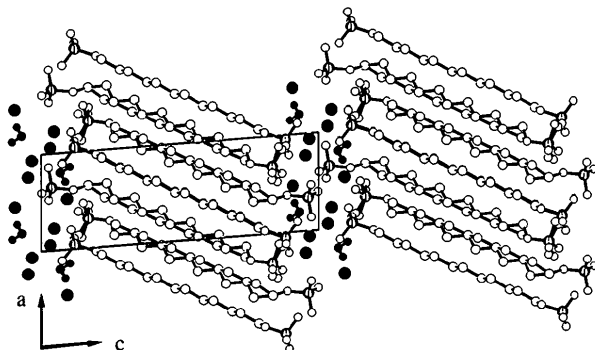


Fig. 2. Layer structure viewed along the direction [010]. Filled circles are Na⁺ cations and water molecules, shaded circles are S atoms. The H atoms of the chains are omitted for clarity.

The Na⁺ cations are sixfold coordinated by sulfate O atoms and the water O atom. To determine the geometry of the coordination polyhedra, a regular octahedron of variable size was fitted to each Na⁺ cation and its coordinated atoms. The maximum deviations of the observed atom positions from the corners of the regular octahedron were 1.012 (2) Å for Na1 (first orientation of the disordered sulfate group), 0.840 (3) Å (second orientation), 0.890 (3) Å for Na2 (first orientation) and 0.878 (2) Å (second orientation). The corresponding distances between the corners and the center of the regular octahedron are 2.372, 2.401, 2.324 and 2.316 Å, respectively. Neither a regular octahedron nor a regular trigonal prism could be fitted to Na3 and its coordinated O atoms. There are two pairs of hydrogen bridges between the water molecule and two disordered sulfate groups. The distances are 3.005 (5)/2.677 (7) to O223/O323 and 2.726 (5)/3.010 (7) Å to O224/O234. The hydrogen bridges connect sulfate groups within the layer; they do not bridge between layers.

The angles between the hydrocarbon chains and the head-group plane (ab) are 50.0, 50.4 and 50.6° for the centrosymmetric molecule and the two disordered

chains, respectively. This means that the area per chain, measured perpendicular to the chain direction, is between 17.8 and 18.0 Å², which is remarkably small. Typical values for chain cross-sections in a crystal are between 18.3 and 19.5 Å² (Abrahamsson, Dahlén, Löfgren & Pascher, 1978). The chain packing is rather unusual. Normally the planes of neighbouring chains are parallel or perpendicular to each other; in the present case, the angles are 73 (1 and 2), 9.9 (1 and 3) and 63° (2 and 3), where 1, 2 and 3 are the planes of the symmetric and the two disordered chains, respectively.

Fig. 3 shows the chain packing. The chains form rows perpendicular to the chain plane of the symmetric molecule. The sequence in these rows is 1–2–3'–1–..., 1–3–2'–1–... or 1–3–3'–1–... (from left to right in Fig. 3). 2' and 3' are centrosymmetrically related to the disordered chains 2 and 3. The sequence 2–2' is not possible in these rows because this would result in interchain C—C distances of about 3.4 Å. There are other rows of chains at an angle of about 70° to the above-mentioned rows with a sequence of 1–2–2'–1–..., 1–2–3'–1–... or 1–3–2'–1–... (from top to bottom in Fig. 3). The sequence 3–3' in these rows would result in C—C distances of about 3.3 Å and is therefore impossible. The sequence 2–2' is improbable because all C—C distance would be greater than 4.7 Å.

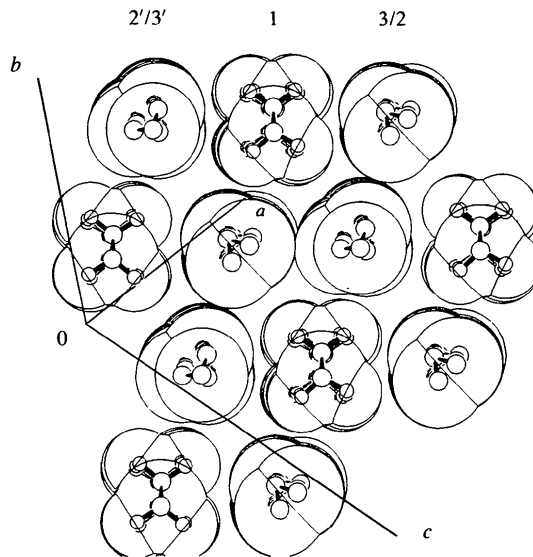


Fig. 3. Chain packing viewed along the chain direction. Of the disordered pairs both parts are shown. The H atoms of the disordered pairs are omitted for clarity. The straight thin lines are the projections of the unit-cell edges. '1' denotes the chain of the symmetric molecule, '2' and '3' the two parts of the disordered chain.

Experimental

Sodium 1,12-dodecylene disulfate was prepared by sulfation of 1,12-dodecanediol (Merck synthesis grade) with chlorosulfonic acid. A suspension was made from the diol in diethyl ether

at 273 K, treated with a 10% molar excess of chlorosulfonic acid (as diethyl ether adduct) per OH group and the obtained sulfuric acid half ester neutralized with 2 N sodium carbonate. The solid was filtered, dissolved in alcohol and filtered again to remove inorganic residues. For purification, the sodium 1,12-dodecylene disulfate was recrystallized several times from alcohol/water (5/1) and determined by elemental analysis (calculated for C₁₂H_{25.33}Na₂O_{8.67}S₂, C 34.45, H 6.10, Na 10.99, S 15.33%; found C 34.37, H 6.25, Na 10.85, S 15.09%).

Crystal data

2Na⁺·C₁₂H₂₄O₈S₂²⁻·2/3H₂O

M_r = 418.42

Triclinic

P $\bar{1}$

a = 7.087 (2) Å

b = 10.2878 (15) Å

c = 19.539 (3) Å

α = 88.820 (12)°

β = 85.49 (2)°

γ = 72.92 (2)°

V = 1357.5 (5) Å³

Z = 3

D_x = 1.535 Mg m⁻³

Data collection

CAD-4 diffractometer

$\theta/2\theta$ scans

Absorption correction:

ψ scans (Fair, 1990)

T_{min} = 0.855, *T_{max}* = 0.998

8230 measured reflections

7435 independent reflections

5198 observed reflections

[*I* > 2σ(*I*)]

Refinement

Refinement on *F*²

$R[F^2 > 2\sigma(F^2)] = 0.0504$

$wR(F^2) = 0.1620$

S = 1.021

7434 reflections

396 parameters

H atoms riding

$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} = -0.122

$\Delta\rho_{\text{max}} = 0.790 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.483 \text{ e \AA}^{-3}$

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Na1	1.2220 (2)	0.06572 (11)	0.04630 (5)	0.0360 (3)
Na2	0.52445 (15)	0.51586 (10)	0.09329 (5)	0.0304 (2)
Na3	1.0592 (2)	0.65384 (12)	0.03259 (7)	0.0477 (3)
O1W	-0.8014 (4)	1.1675 (2)	0.93123 (12)	0.0477 (6)
S11	1.04630 (9)	0.41223 (6)	0.11976 (3)	0.02678 (15)
S21	0.65000 (8)	0.21539 (5)	0.03775 (3)	0.02234 (14)

Mo *K*α radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25

reflections

$\theta = 14-20^\circ$

$\mu = 0.383 \text{ mm}^{-1}$

T = 298 (2) K

Plate

0.66 (2) × 0.11 (2)

× 0.020 (5) mm

Clear

R_{int} = 0.0203

$\theta_{\text{max}} = 29.97^\circ$

h = -1 → 9

k = -13 → 14

l = -27 → 27

3 standard reflections

frequency: 30 min

intensity decay: 1%

S22	-0.30359 (10)	1.16975 (6)	0.83202 (3)	0.0298 (2)
O111	0.9576 (3)	0.4474 (2)	0.19583 (9)	0.0338 (4)
O112	1.1073 (3)	0.2668 (2)	0.11841 (11)	0.0412 (5)
O113	1.2028 (3)	0.4756 (2)	0.10720 (10)	0.0344 (4)
O114	0.8866 (3)	0.4731 (2)	0.07583 (10)	0.0381 (4)
O211	0.6128 (3)	0.2651 (2)	0.11486 (8)	0.0301 (4)
O212	0.6003 (3)	0.3447 (2)	0.00231 (8)	0.0295 (4)
O213	0.8572 (3)	0.1417 (2)	0.02600 (9)	0.0348 (4)
O214	0.5236 (3)	0.1329 (2)	0.02700 (10)	0.0380 (4)
O221	-0.2580 (3)	1.1329 (2)	0.75340 (9)	0.0362 (4)
O222†	-0.4385 (7)	1.3088 (4)	0.8308 (2)	0.0334 (9)
O223†	-0.3834 (6)	1.0773 (4)	0.8678 (2)	0.0365 (10)
O224†	-0.1084 (6)	1.1688 (5)	0.8552 (2)	0.0539 (13)
O322‡	-0.3668 (10)	1.3103 (5)	0.8320 (2)	0.0309 (12)
O323‡	-0.4643 (10)	1.1002 (6)	0.8503 (3)	0.048 (2)
O324‡	-0.1371 (8)	1.1040 (7)	0.8673 (3)	0.051 (2)
C11	0.9203 (4)	0.5892 (3)	0.21697 (13)	0.0357 (6)
C12	0.7978 (4)	0.6094 (3)	0.28397 (14)	0.0366 (6)
C13	0.7740 (4)	0.7497 (3)	0.31371 (14)	0.0384 (6)
C14	0.6476 (5)	0.7744 (3)	0.38134 (14)	0.0401 (6)
C15	0.6344 (4)	0.9089 (3)	0.41552 (14)	0.0386 (6)
C16	0.5065 (4)	0.9330 (3)	0.48257 (14)	0.0383 (6)
C201	0.6460 (5)	0.1613 (3)	0.16726 (13)	0.0394 (7)
C203	0.4805 (4)	0.3364 (3)	0.26101 (13)	0.0386 (6)
C205	0.3281 (5)	0.4954 (3)	0.36221 (14)	0.0435 (7)
C207	0.1797 (5)	0.6520 (3)	0.46383 (15)	0.0443 (7)
C209	0.0333 (5)	0.8108 (3)	0.56476 (15)	0.0437 (7)
C211	-0.1139 (5)	0.9729 (3)	0.66366 (14)	0.0399 (6)
C202§	0.6508 (8)	0.2198 (5)	0.2360 (2)	0.0346 (13)
C204§	0.4838 (10)	0.3695 (6)	0.3360 (3)	0.0367 (13)
C206§	0.3327 (10)	0.5259 (6)	0.4370 (3)	0.0384 (13)
C208§	0.1849 (10)	0.6841 (6)	0.5386 (3)	0.0400 (14)
C210§	0.0363 (11)	0.8448 (6)	0.6394 (3)	0.0394 (14)
C212§	-0.1082 (10)	1.0056 (6)	0.7373 (3)	0.0349 (13)
C302¶	0.5081 (9)	0.2037 (6)	0.2280 (3)	0.0348 (14)
C304¶	0.3640 (12)	0.3632 (6)	0.3276 (3)	0.0381 (15)
C306¶	0.2158 (12)	0.5193 (7)	0.4289 (3)	0.041 (2)
C308¶	0.0693 (11)	0.6758 (6)	0.5316 (3)	0.0372 (14)
C310¶	-0.0761 (11)	0.8332 (6)	0.6336 (3)	0.0372 (14)
C312¶	-0.2164 (12)	0.9904 (6)	0.7333 (3)	0.038 (2)

† Site occupancy factor 0.588 (8).

‡ Site occupancy factor 0.412 (8).

§ Site occupancy factor 0.521 (5).

¶ Site occupancy factor 0.479 (5).

Table 2. Selected geometric parameters (Å, °)

S11—O111	1.574 (2)	C16—C16'	1.525 (5)
S11—O112	1.431 (2)	C201—C202	1.490 (5)
S11—O113	1.446 (2)	C201—C302	1.464 (6)
S11—O114	1.457 (2)	C203—C202	1.488 (6)
S21—O211	1.578 (2)	C203—C204	1.515 (6)
S21—O212	1.449 (2)	C203—C302	1.476 (6)
S21—O213	1.444 (2)	C203—C304	1.470 (6)
S21—O214	1.432 (2)	C205—C204	1.502 (6)
S22—O221	1.575 (2)	C205—C206	1.505 (6)
S22—O222	1.469 (4)	C205—C304	1.476 (6)
S22—O223	1.392 (3)	C205—C306	1.458 (6)
S22—O224	1.486 (4)	C207—C306	1.484 (7)
S22—O322	1.382 (5)	C207—C308	1.470 (6)
S22—O323	1.530 (6)	C207—C206	1.499 (6)
S22—O324	1.402 (6)	C207—C208	1.509 (6)
O111—C11	1.467 (3)	C209—C208	1.495 (6)
O211—C201	1.445 (3)	C209—C210	1.510 (6)
O221—C212	1.445 (5)	C209—C308	1.489 (6)
O221—C312	1.463 (6)	C209—C310	1.485 (6)
C11—C12	1.496 (4)	C211—C210	1.488 (6)
C12—C13	1.526 (4)	C211—C212	1.490 (6)
C13—C14	1.519 (4)	C211—C310	1.506 (6)
C14—C15	1.524 (4)	C211—C312	1.481 (6)
C15—C16	1.515 (4)		

O112—S11—O111	103.46 (11)	C12—C13—C14	112.2 (2)
O113—S11—O111	107.10 (10)	C13—C14—C15	113.7 (2)
O114—S11—O111	106.48 (11)	C14—C15—C16	113.3 (2)
O112—S11—O113	115.72 (12)	C15—C16—C16'	113.6 (3)
O112—S11—O114	113.38 (12)	O211—C201—C202	111.3 (3)
O113—S11—O114	109.88 (12)	O211—C201—C302	111.7 (3)

O212—S21—O211	100.58 (9)	C201—C202—C203	118.2 (4)
O213—S21—O211	107.60 (11)	C202—C203—C204	113.1 (4)
O214—S21—O211	108.40 (11)	C302—C203—C304	117.7 (4)
O213—S21—O212	112.00 (11)	C203—C204—C205	115.5 (4)
O214—S21—O212	114.78 (12)	C204—C205—C206	114.7 (4)
O214—S21—O213	112.49 (12)	C304—C205—C306	119.3 (4)
O322—S22—O221	103.2 (2)	C205—C206—C207	115.5 (4)
O223—S22—O221	111.8 (2)	C206—C207—C208	115.8 (4)
O324—S22—O221	109.2 (2)	C306—C207—C308	119.6 (4)
O222—S22—O221	102.6 (2)	C207—C208—C209	115.4 (5)
O224—S22—O221	103.8 (2)	C208—C209—C210	116.2 (4)
O323—S22—O221	100.0 (2)	C308—C209—C310	117.8 (4)
O223—S22—O222	114.1 (2)	C209—C210—C211	115.0 (4)
O223—S22—O224	112.5 (2)	C210—C211—C212	114.4 (4)
O222—S22—O224	111.1 (2)	C310—C211—C312	114.2 (4)
O322—S22—O323	115.7 (3)	C211—C212—O221	108.5 (4)
O324—S22—O323	108.5 (3)	C201—C302—C203	120.8 (4)
C11—O111—S11	115.8 (2)	C203—C304—C205	119.4 (5)
C201—O211—S21	117.07 (15)	C205—C306—C207	119.4 (4)
C212—O221—S22	115.7 (2)	C207—C308—C209	118.2 (5)
C312—O221—S22	118.1 (3)	C209—C310—C211	115.5 (5)
O111—C11—C12	107.8 (2)	C211—C312—O221	108.1 (4)
C11—C12—C13	110.9 (2)		
O111—C11—C12—C13		173.1 (2)	
O211—C201—C202—C203		53.7 (5)	
O211—C201—C302—C203		-50.6 (6)	
C310—C211—C312—O221		-175.2 (5)	

Symmetry code: (i) $1 - x, 2 - y, 1 - z$.

Structure solution in space group $P1$ gave the same disorder as in $P\bar{1}$, i.e. all atom positions including disordered pairs found in $P\bar{1}$ were also found in $P1$. Therefore, the disorder cannot be explained by a wrong choice of the space group. The positions of H atoms bonded to C atoms were calculated at a distance of 0.97 Å, their U values set to 1.3 times the equivalent U values of their bonding partners, and were refined riding on the C atoms. The H atoms of the water molecules were found from difference Fourier synthesis and refined without constraints. Two independent population parameters were refined, one for the disordered chain, one for the disordered sulfate group. They were 0.479 (5)/0.521(5) for the chain and 0.412 (8)/0.588(8) for the sulfate group. Refinement of the population parameter of the water molecule gave 0.99 (1), therefore it was fixed to 1.0 in the final refinement cycles. After refinement, the highest difference density peak was found near the S atom of the disordered sulfate group.

Data collection: Enraf–Nonius (1977) CAD-4 diffractometer system. Cell refinement: Enraf–Nonius (1977) CAD-4 diffractometer system. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SCHAKAL92* (Keller, 1992). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1176). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two Derivatives of Lithium Isodicyclopentadienide: [(1,2,3,3a,7a- η)-4,5,6,7-Tetrahydro-4,7-methanoindenido](*N,N,N',N'*-tetramethylethylenediamine)lithium and Bis(1,4,7,10-tetraoxacyclododecane)-lithium(1+) Bis[(1,2,3,3a,7a- η)-4,5,6,7-tetrahydro-4,7-methanoindenido]lithate(1-)

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Abstract

Selective crystallization of a solution of lithium isodicyclopentadienide, (isodiCp)Li, in dry thf or diethyl ether under argon has produced two lithium complexes: (isodiCp)Li(TMEDA), [Li(C₁₀H₁₁)(C₆H₁₆N₂)], (4), and [Li(12-crown-4)₂]⁺[Li(isodiCp)₂]⁻, [Li(C₈H₁₆O₄)₂]-[Li(C₁₀H₁₁)₂], (5). In (4) the Li⁺ ion is coordinated to the two N atoms of the disordered TMEDA and is η^5 -coordinated to the Cp ring of the isodiCp ligand. The Li–(Cp ring centroid) distance is 1.906 (7) Å. In (5) there are two independent half-molecules of the anion and one molecule of the cation in the asymmetric unit. In each anion, the Li⁺ ion occupies a crystallographic inversion center and is η^5 -coordinated to the two Cp rings of two isodiCp ligands. The Cp rings are in a staggered arrangement, as required by the inversion center. The Li–(Cp