C(32)	−0.0311 (9)	−0.1137 (10)	0.3969 (5)	0.027 (2)
C(33)	0.0095 (10)	−0.1733 (9)	0.4677 (6)	0.030 (2)
C(34)	0.1407 (10)	−0.1622 (10)	0.4977 (6)	0.032 (2)
C(35)	0.2327 (10)	−0.0877 (11)	0.4566 (6)	0.037 (3)
C(36)	0.1955 (9)	−0.0240 (10)	0.3873 (6)	0.030 (2)

Table 2. *Selected geometric parameters* (Å, °)

Pb(1)—C(31)	2.201 (9)	C(21)—C(22)	1.363 (13)
Pb(1)—C(21)	2.213 (8)	C(21)—C(26)	1.392 (13)
Pb(1)—C(1)	2.214 (8)	C(22)—C(23)	1.397 (13)
Pb(1)—Br(1)	2.985 (2)	C(23)—C(24)	1.39 (2)
Pb(1)—Br(1*a*)	2.885 (2)	C(24)—C(25)	1.36 (2)
C(1)—C(11)	1.484 (12)	C(25)—C(26)	1.387 (14)
C(11)—C(16)	1.396 (14)	C(31)—C(36)	1.375 (12)
C(11)—C(12)	1.406 (14)	C(31)—C(32)	1.388 (12)
C(12)—C(13)	1.370 (14)	C(32)—C(33)	1.383 (13)
C(13)—C(14)	1.370 (15)	C(33)—C(34)	1.361 (14)
C(14)—C(15)	1.38 (2)	C(34)—C(35)	1.383 (14)
C(15)—C(16)	1.385 (13)	C(35)—C(36)	1.372 (14)
C(31)—Pb(1)—C(21)	115.4 (3)	Br(1)—Pb(1)—Br(1a^{i})	173.610 (15)
C(31)—Pb(1)—C(1)	127.8 (3)	Pb(1)—Br(1)—Pb(1b^{ii})	122.73 (5)
C(21)—Pb(1)—C(1)	116.7 (3)	C(11)—C(1)—Pb(1)	113.9 (6)
C(31)—Pb(1)—Br(1a^{i})	87.3 (2)	C(16)—C(11)—C(1)	120.1 (9)
C(21)—Pb(1)—Br(1a^{i})	93.6 (3)	C(12)—C(11)—C(1)	122.1 (9)
C(1)—Pb(1)—Br(1a^{i})	93.4 (3)	C(22)—C(21)—Pb(1)	121.6 (7)
C(31)—Pb(1)—Br(1)	88.6 (2)	C(26)—C(21)—Pb(1)	119.5 (7)
C(21)—Pb(1)—Br(1)	92.6 (3)	C(36)—C(31)—Pb(1)	116.9 (6)
C(1)—Pb(1)—Br(1)	85.3 (3)	C(32)—C(31)—Pb(1)	122.1 (6)

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

Systematic absences ($h0l$) $h + l = 2n + 1$, ($00l$) $l = 2n + 1$ and ($0k0$) $k = 2n + 1$ were detected. The structure was solved by standard Patterson and difference Fourier methods (*SHELXTL-Plus*; Sheldrick, 1987) and refined satisfactorily within space group $P2_1/c$ (No. 14) by full-matrix least-squares calculations (*SHELXL*; Sheldrick, 1994). The H atoms were placed in geometrically calculated positions and refined with common isotropic displacement parameters for different C—H types (H_{aryl}, H_{alkyl}). Computer programs used were *SHELXTL-Plus* (Sheldrick, 1987), *SHELXL*, *PARST* (Nardelli, 1983), *PLATON* (Spek, 1990) and *MISSYM* (Le Page, 1987).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and least-squares-planes data have been deposited with the IUCr (Reference: SH1079). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Hydrate of the Sodium Salt of a Penem Carboxylic Acid

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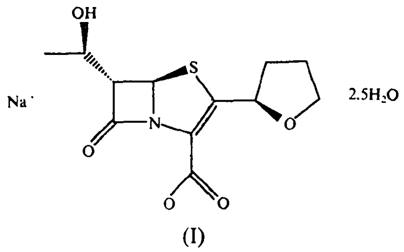
Abstract

The crystal structure of sodium (5*R*,6*S*)-6-[(*R*)-1-hydroxyethyl]-7-oxo-3-[(*R*)-2-tetrahydrofuryl]-4-thia-1-azabicyclo[3.2.0]hept-2-ene-2-carboxylate 2.5-hydrate, $Na^+.C_{12}H_{14}NO_5S^-.\frac{5}{2}H_2O$, a member of a new class of β-lactam antibiotics, has been determined by X-ray diffraction. The C(3)—S(1) bond (bridgehead C atom) is longer than the C(2)—S(1) bond, although the latter is usually longer in penicillins and cephalosporins. The crystal packing shows a three-layer sheet in which two layers of the molecules are held together by Na^+ ions and by water molecules through a network of hydrogen bonds.

Comment

The title compound (I), which has the tetrahydrofuran ring at the C(2) position, shows potent *in vivo* activity by oral administration (Nishino *et al.*, 1991). Knowledge of the accurate crystal structure of this compound should be useful for understanding the interaction of the molecule with water and biological macromolecules.



(I)

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The bond lengths and angles of the penem nucleus and the carboxyl group of this molecule are similar to those of other penems. Those of the tetrahydrofuran ring are also similar to those found for tetrahydro-2-furancarboxylic acid (Bando, Takano, Tanaka, Iwata & Ishiguro, 1990). The β-lactam ring of the penem has a puckered structure like those of penicillins and cephalosporins. This is different from the conformations of unfused β-lactams, the rings of which are usually flat (Bando *et al.*, 1989). The angle C(3)—S(1)—C(2) of 90.7 (2)° is smaller than the corresponding average angle of 94.2 (18)° for 14 cephalosporins and is close to the average angle of 90.6 (8)° for seven penicillins of the ampicillin type obtained through a search of the Cambridge Structural Database (Allen *et al.*, 1979). In the penem the C(3)—S(1) bond [1.831 (4) Å] is longer than the C(2)—S(1) bond [1.775 (5) Å], whereas in the penicillins and the cephalosporins the C(2)—S(1) bond is longer [averages 1.85 (1) and 1.83 (2) Å, respectively] than the C(3)—S(1) bond [average 1.80 (1) Å for each]. This characteristic difference in the bond lengths could be the reason for the unusual reactivity of the penem in photolysis (Iwata, Tanaka, Oyama & Ishiguro, 1991), alkaline hydrolysis (Iwata, Tanaka & Ishiguro, 1990) and biological hydrolysis.

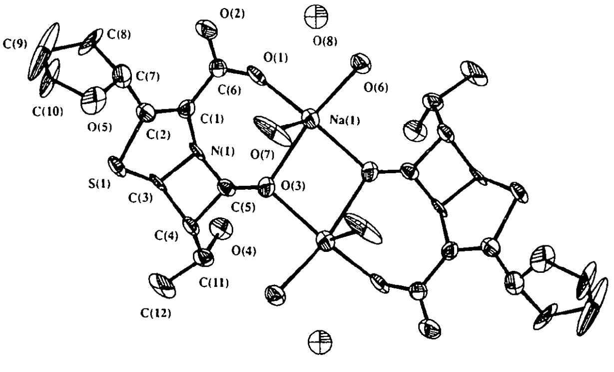

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecular structure with atom-numbering scheme. The ellipsoids correspond to 50% probability levels of atomic displacement.

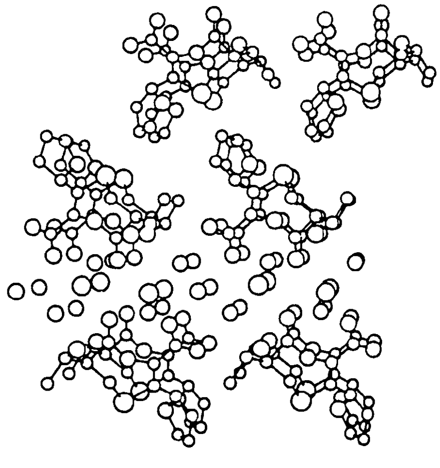

Fig. 2. *PLUTO* (Motherwell & Clegg, 1978) drawing of the crystal packing.

The C—O bonds of the carboxylate group are intermediate between single- and double-bonds. This indicates that the group is deprotonated and that electron delocalization occurs, although the C(6)—O(1) bond [1.281 (6) Å] is longer than the C(6)—O(2) bond by 0.05 Å. The C(5)—O(3) bond [1.215 (5) Å] is slightly longer than the corresponding average bond length [1.19 (2) Å] for five penems obtained from the Cambridge Structural Database as a result of the coordination of O(1) and O(3) to Na(1).

The structure contains pairs of Na$^+$ cations, each pair being bridged by two β-lactam carbonyl groups. The distorted trigonal-bipyramidal coordination geometry around each Na$^+$ is completed by coordination to one of the carboxylate O atoms [O(1)] and to the O atoms [O(6) and O(7)] from two of the water molecules. These water molecules are also hydrogen bonded to the carbonyl, carboxylate and hydroxyethyl groups of the penem. The water O atom O(8) is hydrogen bonded to a carboxylate group and to O(6). The coordination to the Na$^+$ cations and the hydrogen bonds link two layers of penem molecules to form a three-layer sheet. There are no interactions between the sheets except for van der Waals contacts.

Experimental

Crystal data

Na$^+$.C$_{12}$H$_{14}$NO$_5$S$^-$.$\frac{5}{2}$H$_2$O
M_r = 352.3
Orthorhombic
$P2_12_12$
a = 9.208 (1) Å
b = 32.454 (2) Å
c = 5.495 (3) Å
V = 1642.1 (10) Å^3
Z = 4
D_x = 1.43 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 45 reflections
θ = 19–32°
μ = 2.307 mm^{-1}
T = 293 K
Hexagonal plate
0.5 × 0.3 × 0.3 mm
Colourless

Data collection

Rigaku AFC-5 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1606 measured reflections
1606 independent reflections
1592 observed reflections [$F > 3\sigma(F)$]

$\theta_{\max}$ = 63°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 38$
$l = 0 \rightarrow 6$
3 standard reflections monitored every 100 reflections intensity variation: 0.8%

Refinement

Refinement on F
R = 0.059
wR = 0.110

$(\Delta/\sigma)_{\max}$ = 4.84
$\Delta\rho_{\max}$ = 0.51 e Å^{-3}
$\Delta\rho_{\min}$ = −0.27 e Å^{-3}

$S = 1.92$
1592 reflections
204 parameters
H atoms not located
$w = 1/[\sigma^2(F_o) + 0.02081F_o + 0.0049F_o^2]$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S(1)	0.0444 (1)	0.3203 (1)	0.8346 (2)	0.040
Na(1)	0.1888 (2)	0.4939 (1)	0.8123 (4)	0.039
O(1)	0.3208 (3)	0.4459 (1)	1.0278 (6)	0.037
O(2)	0.4625 (3)	0.4015 (1)	0.8265 (9)	0.051
O(3)	−0.0239 (3)	0.4535 (1)	0.9042 (6)	0.035
O(4)	−0.1491 (4)	0.4125 (1)	1.4301 (7)	0.044
O(5)	0.2486 (5)	0.2999 (1)	0.4651 (8)	0.058
O(6)	0.3569 (3)	0.5397 (1)	0.6595 (7)	0.040
O(7)	0.1504 (6)	0.4599 (2)	0.4524 (9)	0.086
O(8)	1/2	1/2	0.2681 (9)	0.047
N(1)	0.0889 (4)	0.3919 (1)	1.0352 (7)	0.030
C(1)	0.2221 (4)	0.3828 (1)	0.9117 (9)	0.032
C(2)	0.2119 (5)	0.3464 (1)	0.7922 (9)	0.037
C(3)	−0.0071 (4)	0.3566 (1)	1.0747 (8)	0.030
C(4)	−0.1405 (4)	0.3854 (1)	1.0266 (8)	0.030
C(5)	−0.0240 (5)	0.4179 (1)	0.9725 (7)	0.029
C(6)	0.3459 (5)	0.4116 (1)	0.9209 (9)	0.032
C(7)	0.3233 (6)	0.3255 (1)	0.639 (1)	0.045
C(8)	0.4265 (7)	0.2979 (2)	0.777 (2)	0.072
C(9)	0.398 (2)	0.2559 (3)	0.671 (3)	0.173
C(10)	0.317 (1)	0.2611 (2)	0.462 (2)	0.083
C(11)	−0.2373 (4)	0.3964 (1)	1.2395 (8)	0.034
C(12)	−0.3233 (6)	0.3592 (2)	1.327 (1)	0.062

Table 2. *Selected geometric parameters* (Å, °)

S(1)—C(2)	1.775 (5)	Na(1)···O(7)	2.292 (6)
S(1)—C(3)	1.831 (4)	O(6$^{\rm ii}$)···O(2)	2.691 (6)
O(1)—C(6)	1.281 (6)	O(6$^{\rm ii}$)···O(4$^{\rm iii}$)	2.766 (5)
O(2)—C(6)	1.235 (7)	O(7)···O(1$^{\rm iv}$)	2.848 (7)
O(3)—C(5)	1.215 (5)	O(7)···O(3)	2.963 (7)
Na(1)···O(1)	2.304 (4)	O(7)···O(4$^{\rm iv}$)	3.160 (7)
Na(1)···O(3)	2.410 (4)	O(8)···O(1$^{\rm iv}$)	2.748 (6)
Na(1)···O(3$^{\rm i}$)	2.340 (4)	O(8)···O(6)	2.833 (6)
Na(1)···O(6)	2.305 (4)		
C(2)—S(1)—C(3)	90.7 (2)		

Symmetry codes: (i)$-x, -y+1, z$; (ii) $-x+1, -y+1, z$; (iii) $x+1, y, z-1$; (iv) $x, y, z-1$.

The high values of wR and $(\Delta/\sigma)_{\rm max}$ result from disorder of the tetrahydrofuryl group, the hydroxyethyl group and the water O atom (O7). Data collection: *AFC-5 Data Collection Software* (Rigaku Corporation, 1984*a*). Data reduction: *RASA-5P* (Rigaku Corporation, 1984*b*). Program(s) used to solve structure: *MULTAN*11/84 (Main, Germain & Woolfson, 1984). Program(s) used to refine structure: *RASA-5P*. Molecular graphics: *ORTEP* (Johnson, 1965); *PLUTO* (Motherwell & Clegg, 1978) .

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: AS1108). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Di-μ-chloro-bis[dichlorotris(2-propanol)cerium(III)] at 153 K

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Abstract

The structure of di-μ-chloro-bis[dichlorotris(2-propanol)cerium(III)], $[CeCl_3(C_3H_8O)_3]_2$, is reported. The Ce atoms are bridged by two Cl atoms and so a dimer is formed.

Comment

The addition of trimethylsilylpropargyl† magnesium bromide to aldehyde affords, predominantly, allenyl alcohol. The regioselectivity changes dramatically when

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† Propargyl = 2-propynyl.