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Methyl 2,3-dideoxy-2-*S*-methylmercurio-2-thio-*β*-D-*manno*-oct-2-ulopyranosonate-(2,6)

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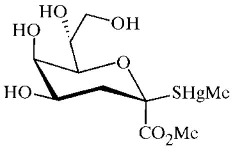
The hexopyranosyl ring of the title compound, $[Hg(CH_3)(C_9H_{15}O_7S)]$, adopts the $^4C_1$ chair conformation, and the anomeric configuration of the thiomethylmercury linkage is *β*. The compound exists as two symmetry-independent conformers, *A* and *B*, within the unit cell, and each shows an almost linear S—Hg—C arrangement. Most of the bond distances and angles in *A* and *B* are similar, although a marked difference exists in the side-chain conformation. Weak secondary intramolecular (between Hg and ring O) and intermolecular (between *A* and *B* conformers) interactions are documented.

Comment

For structure–function studies of glycosidases, we have recently reported the synthesis of a series of mono- and disaccharides, in which methylmercury or phenylmercury is covalently attached to anomeric thioglycosides (Belakhov *et al.*, 2000). It was predicted that examination of these compounds, in the form of stable binary complexes with appropriate enzymes, would provide both the specific binding and the heavy-atom derivative for complete X-ray analysis. Indeed, the similar thiomercuric analogues of sialic acid were used to determine the crystallographic phases for pertussis toxin (Shigeta *et al.*, 1994), and 9-*O*-acetylsialic acid esterase (Fitz *et al.*, 1996) from influenza C virus. The title thiomercuric derivative, (I), was designed as a model compound for a structure–function study of enzymes involved in the biosynthetic formation and utilization of 3-deoxy-D-*manno*-2-octulosonic acid (Kdo). This unique eight-carbon sugar is a specific constituent of the lipopolysaccharides of most Gram-negative bacteria, and is required by them for growth and virulence (Unger, 1981; Unger & Anderson, 1983). Several groups have therefore pursued inhibition of Kdo metabolism as a strategy for the development of novel antibacterial drugs (Hammond *et al.*, 1987; Goldman *et al.*, 1987; Baasov & Kohen, 1995; Liang *et al.*, 1998; Du *et al.*, 1999). As part of this programme, the crystal structure of the title compound, (I), has been determined.

Interestingly, an analysis of the crystallographic data reveals that (I) exists as two symmetry-independent molecules, *A* and *B*, within the unit cell. A view of conformer *A* of the molecule of (I), together with the atomic numbering scheme, is shown in Fig. 1. The geometry observed for the pyranose ring is a $^4C_1$ chair, while the thiomercury moiety is oriented *cis* to the hydroxyl groups at positions C4 and C5, indicating the *β*-anomeric configuration. The Hg atom has an almost linear stereochemistry, with normal Hg—S and Hg—C distances, and S—Hg—C angles of 175.7 (15) and 176.7 (10)° for the two conformers (Table 1). These values are in agreement with those found for CH_3—Hg—S moieties in the Cambridge Structural Database (CSD, April 2001 Release; Allen & Kennard, 1993).



(I)

As illustrated in Fig. 2, while most of the bond distances and angles in conformers *A* and *B* are very similar, marked differences exist at the thiomethylmercury side-chain conformation. This is clearly seen by comparing three torsion angles, C1—C2—S—Hg, C3—C2—S—Hg and O1—C2—S—Hg, which show differences of 15.7 (11), 18.1 (10) and 16.1 (10)°, respectively (Table 1).

The presence of two similar independent structures, *A* and *B*, has also been reported for other thiomercury derivatives (Kuz'mina & Struchkov, 1984; Tasende *et al.*, 1990; Zukerman-Schpector *et al.*, 1991; Varela *et al.*, 1993; Bravo *et al.*, 1985; Castano *et al.*, 1991; Hutton *et al.*, 1980). This phenomenon was

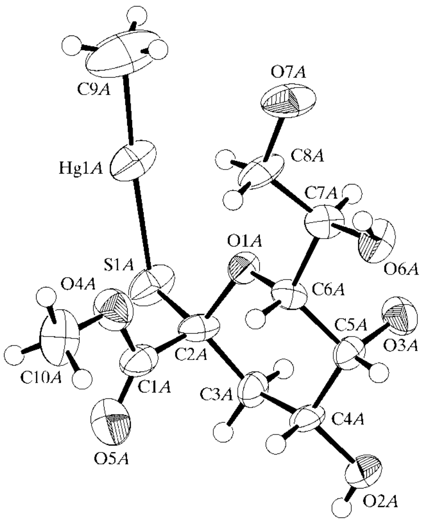


Figure 1
A view of molecule *A* of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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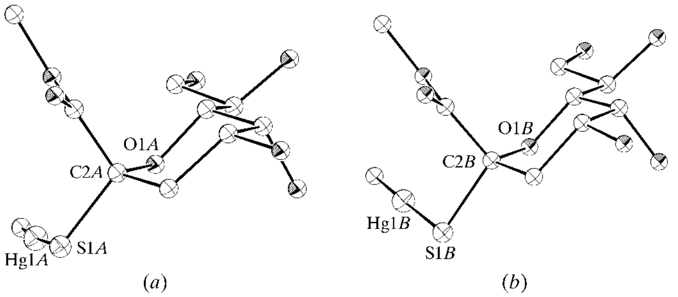

Figure 2
Views of the chair conformations of (*a*) molecule *A* and (*b*) molecule *B*.

attributed to a low residual Lewis acidity of Hg in these complexes, leading to the formation of 'secondary bonds' that are intermediate in strength between covalent and van der Waals bonds (Kuz'mina & Struchkov, 1984). Indeed, the intramolecular Hg···O1 distances in molecules *A* and *B* of (I) were found to be 2.955 (11) and 3.155 (11) Å, respectively. These distances are smaller than the sum of the van der Waals radii for the atoms concerned, confirming the presence of a secondary interaction in this part of the molecule, similar to that observed in (2-mercaptobenzothiazolato)methylmercury(II) (Bravo *et al.*, 1985) and (2-mercaptobenzooxazolato)methylmercury(II) (Castano *et al.*, 1991).

It is of note that, in the latter compound, in addition to an intramolecular Hg···N interaction, an additional intermolecular Hg···O interaction was also observed. In compound (I), however, if we take the values of 3.35 and 3.10 Å for Hg···S and Hg···O as the sums of the van der Waals radii of Hg and S, and Hg and O, respectively (Kuz'mina & Struchkov, 1984), no additional secondary interactions through the Hg atom are observed. This may be due to the presence of an intermolecular hydrogen-bonding network (Table 2). There are rather strong hydrogen bonds both between the molecules of each conformer (O2*A*—H···O7*A* and O2*B*—H···O7*B*), and between the two different conformers (O6*A*—H···O3*B* and O6*B*—H···O3*A*). Because of the presence of these hydrogen bonds, the crystal can be regarded as being made up of a three-dimensional network.

Experimental

Compound (I) was synthesized according to the reported procedure of Belakhov *et al.* (2000), and its purity was established by a combination of ^{1}H NMR, ^{13}C NMR, 2D-COSY, and mass spectroscopic analyses. X-Ray quality crystals of (I) were obtained by recrystallization from a methanol solution.

Crystal data

$[\mathrm{Hg(CH_3)(C_9H_{15}O_7S)}]$
$M_r = 482.89$
Monoclinic, $P2_1$
$a = 7.306\ (1)$ Å
$b = 15.247\ (3)$ Å
$c = 13.014\ (2)$ Å
$\beta = 91.10\ (3)°$
$V = 1449.4\ (4)$ Å^3
$Z = 4$

$D_x = 2.213$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 19 347 reflections
$\theta = 1.2$–$25.4°$
$\mu = 10.79$ mm^{-1}
$T = 293\ (2)$ K
Plate, colourless
$0.10 \times 0.10 \times 0.02$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{\min} = 0.388$, $T_{\max} = 0.806$
11 530 measured reflections

5084 independent reflections
4777 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.058$
$\theta_{\max} = 25.1°$
$h = -8 \rightarrow 8$
$k = -18 \rightarrow 18$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.172$
$S = 1.06$
5084 reflections
349 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0956P)^2 + 11.7784P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.009$
$\Delta\rho_{\max} = 4.38$ e Å^{-3}
$\Delta\rho_{\min} = -1.78$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0040 (7)
Absolute structure: (Flack, 1983), 2408 Friedel pairs
Flack parameter = 0.010 (19)

Table 1
Selected geometric parameters in the two conformers of (I) (Å, °).

	Conformer *A*	Conformer *B*
Hg—C9	2.04 (3)	2.05 (4)
Hg—S	2.346 (6)	2.362 (5)
S—C2	1.798 (17)	1.850 (18)
S—Hg—C9	175.7 (15)	176.7 (10)
Hg—S—C2	99.3 (6)	98.8 (6)
S—C2—C3	108.0 (11)	107.5 (12)
S—C2—O1	108.0 (10)	107.0 (11)
C1—C2—S—Hg	88.7 (11)	73.0 (10)
C3—C2—S—Hg	−149.8 (11)	−167.9 (9)
O1—C2—S—Hg	−31.8 (12)	−47.9 (11)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2*A*—H2O*A*···O7*A*$^{\rm i}$	0.82	2.15	2.87 (2)	146
O6*A*—H6O*A*···O3*B*$^{\rm ii}$	0.78	2.01	2.75 (2)	158
O2*B*—H2O*B*···O7*B*$^{\rm iii}$	0.83	2.06	2.75 (2)	141
O6*B*—H6O*B*···O3*A*$^{\rm iv}$	0.94	1.88	2.81 (2)	168

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

Because the crystal was a very small colourless plate, it was impossible to obtain an accurate measurement of the crystal faces. A little splitting was also found in some of the reflections and *TWIN* options (*SHELXL*97; Sheldrick, 1997) were used in the final refinement. Initially, the positions of the H atoms of the donor atoms were generated as idealized OH groups. During the refinement, the coordinates of atoms H2O*A* and H2O*B* were treated as riding on their parent atoms (O2*A* and O2*B*, respectively). Attempts to find the H atoms on atoms O3 and O7, using *HFIX* 81 or *HFIX* 147 options (*SHELXL*97), failed because, even in idealized positions, short contacts between donor and acceptor H atoms were found (H7*A*···H2O*A* 1.81 Å and H3*B*···H6O*A* 1.51 Å). The choice between which atoms were donors and which acceptors was based on measurement of the O—H···O angles. Short O···O distances, involving atoms O3 or O7, except for those listed in Table 2, were 2.74 (2) and 2.76 (2) Å for O3*A*···O2*B*($2 - x$, $y + \frac{1}{2}$, $2 - z$) and O7*B*···O7*A*($2 - x$, $y + \frac{1}{2}$, $2 - z$).

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *TEXSAN* (Molecular Structure Corporation, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1066). Services for accessing these data are described at the back of the journal.

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