

N21—H212...O12 ⁱⁱ	0.84 (4)	2.03 (4)	2.788 (5)	151 (4)
N22—H221...N12 ⁱⁱⁱ	0.82 (4)	2.74 (4)	3.526 (6)	161 (4)
N22—H222...O12 ⁱⁱ	0.75 (4)	2.28 (4)	2.984 (5)	156 (4)

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

The intensity data were collected for a monoclinic unit cell with $a = 13.419$ (3), $b = 15.733$ (4), $c = 10.573$ (4) Å, $\beta = 113.19$ (2)°. During refinement the unit cell was transformed to higher orthorhombic symmetry; the transformation matrix was $M = (201/001/0\bar{1}0)$. The position of the H atoms of thiourea were refined with a common isotropic temperature factor U_{iso} , whereas for the H atoms of the phenyl rings, a riding model was used while refining common U_{iso} 's.

Data collection: CAD-4L diffractometer software. Cell refinement: CAD-4L diffractometer software. Data reduction: *LOPOTRI* (Gravereau, 1982). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1071). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Sodium Bumetanide Trihydrate

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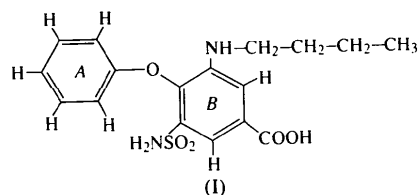
(Received 18 November 1993; accepted 21 April 1994)

Abstract

The structure of sodium 3-(aminosulfonyl)-5-(butylamino)-4-phenoxybenzoate trihydrate (sodium bumetanide trihydrate), $\text{Na}^+ \cdot \text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_5\text{S}^- \cdot 3\text{H}_2\text{O}$, consists of a layer of sodium ions and water molecules between two layers of bumetanide molecules. Six-coordinate Na^+ ions linked by water molecules are arranged in columns parallel to **b**.

Comment

The loop diuretic bumetanide is a powerful inhibitor of the Na^+ , K^+ , Cl^- cotransport system in a variety of epithelial cells (Petzinger, Muller, Follmann, Deutscher & Kinne, 1989). Bumetanide, (I), is a competitive inhibitor of sodium-dependent taurocholate uptake into hepatocytes (Blitzer, Tatoosh, Donovan & Boyer, 1982). The solid-state structures of the bile acids and taurocholate have been reported (Campanelli, Candeloro, Giglio & Scaramuzza, 1987). We undertook the X-ray analysis of sodium bumetanide trihydrate, reported here, as part of our studies of the structures of bioactive molecules.



The molecular structure of the organic moiety is shown in Fig. 1. The geometrical parameters of the bumetanide molecule are unexceptional and in agreement with literature data for similar moieties. This analysis indicates that the N2—C5 bond has partial double-bond character. Bumetanide assumes a 'U' shape with ring A and the alkyl chain forming a hydrophobic region. The packing of the bumetanide molecules with the sodium ions and the water molecules is shown in Fig. 2. The structure consists of a layer of sodium ions and water molecules between two layers of bumetanide molecules with the carboxylic groups oriented towards

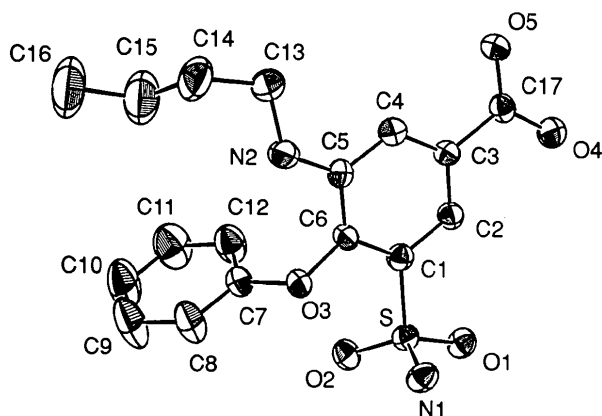


Fig. 1. A view of the molecule showing the labelling of the non-H atoms. Displacement ellipsoids are drawn at the 50% probability level.

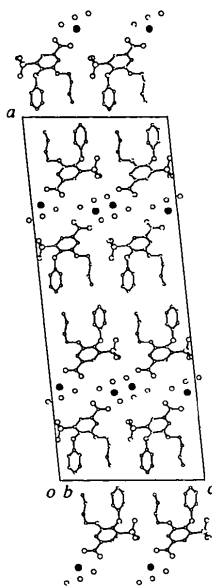


Fig. 2. The packing of the bumetanide molecules viewed down *b*. The Na atoms are drawn as filled circles.

the solvent molecules. Packing is characterized by columns of water-bridged Na^+ ions arranged parallel to *b*. Centrosymmetric pairs of Na^+ ions are bridged by two water molecules (*Ow*1 and *Ow*2); these symmetry-related water molecules link alternate pairs of bridged Na^+ ions along the columns with $\text{Na}^+ \cdots \text{Ow}$ distances in the range 2.367 (4)–2.547 (4) Å. In addition, another water molecule (*Ow*3) and the carboxylic atom *O*5 of the bumetanide bind to Na^+ ions [$\text{Na}^+ \cdots \text{O5}$ 2.462 (3), $\text{Na}^+ \cdots \text{Ow3}$ 2.357 (4) Å] making each Na^+ ion hexacoordinate. The *Ow*3 water molecule occupies the equatorial position in such a way that the pattern of the coordinating atoms appears to be distorted square bipyramidal. The geometric parameters of the hexacoordination and the distances between Na^+ pairs are in agreement with those in the literature (Macdonald, Morrison & Murray, 1991). Adjacent $\text{Na}^+ \text{--H}_2\text{O}$ columns are linked through $\text{Na}^+ \cdots \text{O5}$ (carboxylic) contacts and several hydrogen bonds involving water molecules and carboxylic O atoms belonging to symmetry-related units. A summary of these hydrogen bonds is presented in Table 3 and in Fig. 3.

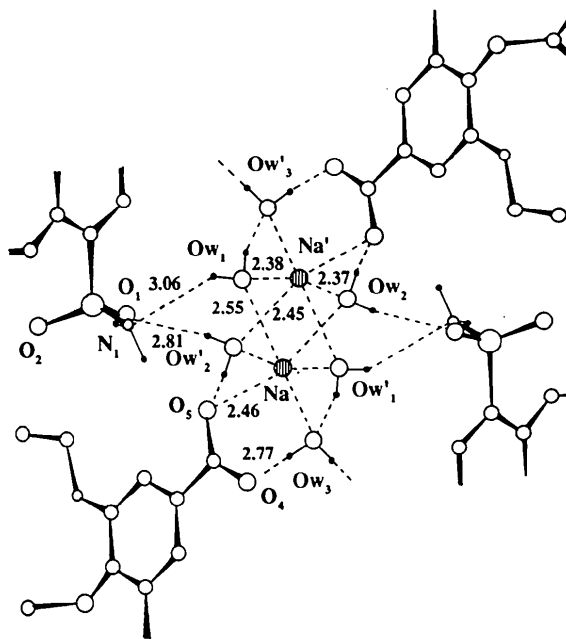


Fig. 3. Part of the structure of sodium bumetanide trihydrate viewed approximately perpendicular to the *ac* plane showing the atom-numbering scheme and interatomic distances (Å) around the Na atom and the water molecules.

Experimental

Crystal data

$\text{Na}^+ \cdot \text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_5\text{S}^- \cdot 3\text{H}_2\text{O}$
 $M_r = 440.44$

Cu $K\alpha$ radiation
 $\lambda = 1.5418 \text{ \AA}$

Monoclinic
C2/c
 $a = 44.819 (2) \text{ \AA}$
 $b = 5.3639 (8) \text{ \AA}$
 $c = 17.694 (4) \text{ \AA}$
 $\beta = 95.91 (2)^\circ$
 $V = 4231.2 (9) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.383 \text{ Mg m}^{-3}$

Cell parameters from 25 reflections
 $\theta = 20\text{--}24^\circ$
 $\mu = 1.930 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
Needle
 $0.5 \times 0.4 \times 0.2 \text{ mm}$
Colourless

Data collection

Enraf–Nonius CAD-4F diffractometer
 ω – 2θ scans
Absorption correction: none
8089 measured reflections
3857 independent reflections
2913 observed reflections
 $[I \geq 3.0\sigma(I)]$

$\theta_{\max} = 70^\circ$
 $h = -54 \rightarrow 54$
 $k = 0 \rightarrow 6$
 $l = 0 \rightarrow 21$
2 standard reflections
frequency: 60 min
intensity decay: 3%

Refinement

Refinement on F^2
 $R = 0.058$
 $wR = 0.059$
 $S = 3.17$
2913 reflections
338 parameters
Only coordinates of H atoms refined

$w = 1/\sigma^2(F_o)$
 $(\Delta/\sigma)_{\max} = 0.19$
 $\Delta\rho_{\max} = 0.17 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.20 \text{ e \AA}^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
S	0.64344 (2)	0.0596 (2)	0.04043 (5)	2.37 (2)
O1	0.66115 (6)	0.2730 (5)	0.0242 (2)	2.87 (6)
O2	0.61218 (6)	0.0690 (6)	0.0143 (2)	3.23 (6)
N1	0.66074 (8)	-0.1786 (7)	0.0090 (2)	2.98 (7)
C1	0.64801 (8)	0.0058 (8)	0.1391 (2)	2.33 (8)
C2	0.66848 (8)	0.1482 (8)	0.1852 (2)	2.52 (8)
C3	0.67240 (8)	0.0975 (8)	0.2623 (2)	2.37 (8)
C4	0.65605 (9)	-0.0918 (8)	0.2928 (2)	2.72 (8)
C5	0.63553 (8)	-0.2366 (8)	0.2467 (2)	2.51 (8)
C6	0.63193 (8)	-0.1855 (8)	0.1695 (2)	2.44 (8)
O3	0.61406 (6)	-0.3377 (5)	0.1209 (2)	2.70 (6)
C7	0.58273 (9)	-0.3077 (9)	0.1180 (2)	2.91 (9)
N2	0.61877 (8)	-0.4221 (8)	0.2744 (2)	3.50 (8)
O4	0.71174 (6)	0.3918 (6)	0.2805 (2)	3.65 (7)
O5	0.69608 (6)	0.2202 (6)	0.3837 (2)	2.91 (6)
C8	0.5696 (1)	-0.119 (1)	0.1524 (3)	4.3 (1)
C9	0.5383 (1)	-0.106 (1)	0.1462 (4)	6.0 (1)
C10	0.5216 (1)	-0.279 (1)	0.1066 (4)	6.2 (2)
C11	0.5351 (1)	-0.472 (1)	0.0723 (4)	6.3 (2)
C12	0.5663 (1)	-0.489 (1)	0.0778 (3)	4.4 (1)
C13	0.6179 (1)	-0.475 (1)	0.3536 (2)	3.8 (1)
C14	0.5946 (1)	-0.673 (1)	0.3649 (3)	5.4 (1)
C15	0.5630 (1)	-0.598 (2)	0.3409 (4)	7.0 (2)
C16	0.5406 (2)	-0.797 (2)	0.3567 (5)	8.9 (2)
C17	0.69516 (8)	0.2470 (8)	0.3127 (2)	2.46 (8)
Na	0.74152 (4)	-0.0007 (3)	0.43756 (9)	2.99 (3)
Ow1	0.77266 (6)	0.3570 (6)	0.4337 (2)	3.60 (7)
Ow2	0.71680 (6)	0.6309 (6)	0.4704 (2)	3.15 (6)
Ow3	0.75300 (6)	0.7497 (6)	0.3348 (2)	3.38 (6)

Table 2. Selected geometric parameters (\AA , $^\circ$)

S—O1	1.439 (3)	O3—C7	1.409 (5)
S—O2	1.430 (3)	C7—C8	1.347 (7)
S—N1	1.622 (4)	C7—C12	1.373 (7)
S—C1	1.760 (4)	N2—C13	1.434 (6)
C1—C2	1.392 (5)	C13—C14	1.516 (8)
C1—C6	1.394 (6)	C17—O4	1.252 (5)
C2—C3	1.386 (5)	C17—O5	1.261 (5)
C3—C4	1.393 (6)	C8—C9	1.398 (7)
C3—C17	1.514 (5)	C9—C10	1.343 (9)
C4—C5	1.400 (6)	C10—C11	1.372 (8)
C5—C6	1.386 (5)	C11—C12	1.394 (7)
C5—N2	1.368 (6)	C14—C15	1.494 (8)
C6—O3	1.381 (5)	C15—C16	1.51 (1)
O1—S—O2	116.7 (2)	C4—C3—C17	120.5 (3)
C5—N2—C13	124.4 (4)	O1—S—N1	105.4 (2)
C3—C4—C5	121.3 (4)	N2—C13—C14	110.8 (4)
O1—S—C1	108.6 (2)	C4—C5—C6	117.9 (4)
C3—C17—O4	117.1 (3)	O2—S—N1	113.8 (2)
C4—C5—N2	123.1 (4)	C3—C17—O5	118.5 (4)
O2—S—C1	109.6 (2)	C6—C5—N2	119.0 (3)
O4—C17—O5	124.4 (4)	N1—S—C1	101.5 (2)
C1—C6—C5	121.0 (4)	C7—C8—C9	118.9 (5)
S—C1—C2	119.6 (3)	C1—C6—O3	118.9 (3)
C8—C9—C10	120.7 (6)	S—C1—C6	119.5 (3)
C5—C6—O3	119.9 (4)	C9—C10—C11	120.1 (5)
C2—C1—C6	120.9 (3)	C6—O3—C7	117.8 (3)
C10—C11—C12	120.2 (5)	C1—C2—C3	118.6 (4)
O3—C7—C8	123.3 (4)	C7—C12—C11	118.2 (5)
C2—C3—C4	120.4 (3)	O3—C7—C12	114.7 (4)
C13—C14—C15	114.9 (5)	C2—C3—C17	119.1 (4)
C8—C7—C12	122.0 (4)	C14—C15—C16	112.8 (6)
N1—S—C1—C2	105.3 (3)	O1—S—C1—C2	-5.4 (4)
C4—C5—N2—C13	6.3 (7)	C1—C6—O3—C7	-107.2 (4)
C6—O3—C7—C8	8.9 (6)	C5—N2—C13—C14	173.9 (4)
N2—C13—C14—C15	-64.8 (6)	C2—C3—C17—O4	-7.6 (6)

Table 3. Intermolecular hydrogen bonds (\AA , $^\circ$) and contact distances (\AA) around the Na^+ ion

$D\cdots H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$	
N1—H1 \cdots O1 ⁱ	2.954 (5)	154 (5)	
N1—H2 \cdots O5 ⁱⁱ	2.863 (5)	148 (4)	
Ow1—H21 \cdots N1 ⁱⁱⁱ	3.058 (4)	121 (5)	
Ow1—H20 \cdots Ow3	2.821 (5)	168 (5)	
Ow2—H23 \cdots O1 ^{iv}	2.807 (4)	162 (5)	
Ow2—H22 \cdots O5	2.788 (5)	169 (5)	
Ow3—H25 \cdots O4	2.768 (4)	158 (5)	
Ow3—H24 \cdots O4 ⁱⁱⁱ	2.811 (5)	174 (4)	
Na \cdots Na ^v	3.514 (2)	Na \cdots Ow2 ⁱ	3.367 (4)
Na \cdots Na ^{vi}	3.502 (2)	Na \cdots Ow2 ^v	3.450 (4)
Na \cdots Ow1	3.378 (4)	Na \cdots Ow3 ⁱ	3.357 (4)
Na \cdots Ow1 ^v	3.547 (4)	Na \cdots O5	3.462 (3)

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

The structure was solved using *MULTAN80* (Main *et al.*, 1980) and refined by blocked full-matrix least squares with anisotropic displacement parameters for all non-H atoms. H atoms were located on the ΔF map and included in the structure-factor calculation with the isotropic temperature factors of their carrier atoms. All calculations were performed using *SDP* software (Enraf–Nonius, 1986) on a MicroVAX 3100 computer.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: NA1078). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Trimethylammonium Tin Sulfide

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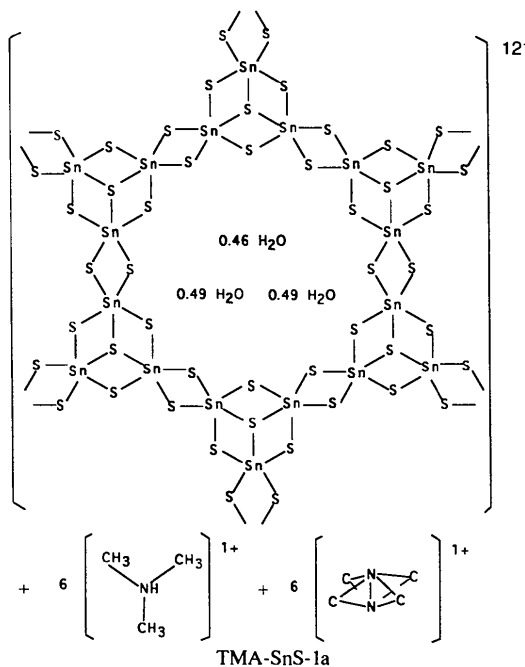
Abstract

The structure of trimethylammonium tin sulfide-water (1/0.72), [(CH₃)₃NH]₂[Sn₃S₇]·0.72H₂O, consists of sheets with 24-membered ring openings containing alternating Sn and S atoms. Organic molecules resulting from the breakdown of the starting tetramethylammonium template reside between these sheets, which are stacked parallel to (001).

Comment

Crystalline microporous metal sulfides form a novel family of open framework materials (Bedard, Wilson, Vail, Bennett & Flanigen, 1989; Bedard, Vail, Wilson & Flanigen, 1989, 1990). The structural details of some of the antimony (Dittmar & Schäfer, 1978; Eisenmann & Schäfer, 1979; Sheldrick & Häusler, 1988; Parise, 1990, 1991; Parise & Ko, 1992; Tan, Ko & Parise, 1994), tin (Sheldrick, 1988; Ko, Cahill & Parise, 1994; Parise, Ko, Rijssenbeek, Nellis, Tan & Koch, 1994) and

germanium sulfides (Bedard, Wilson, Vail, Bennett & Flanigen, 1989) have been reported. Recently, Parise, Ko, Rijssenbeek, Nellis, Tan & Koch (1994) solved the structure of tetramethylammonium tin sulfide (TMA-SnS-1) (Bedard, Vail, Wilson & Flanigen, 1989). This substance was synthesized hydrothermally from slurries of SnS₂, tetramethylammonium hydroxide (TMA-OH), elemental S and H₂O. It has a framework similar to that described by Sheldrick & Braunbeck (1990) for the alkali metal selenide analogue CS₂Sn₃Se₇. Here, we report a closely related compound obtained after prolonged heating of the same organic template (TMA-OH) but with different Sn and S reactants. The new structure is designated TMA-SnS-1a.



The primary building unit for TMA-SnS-1a is a [SnS₅]⁶⁻ trigonal bipyramid, which is common in both open and dense tin sulfide frameworks (Krebs, 1983). The secondary building unit (Fig. 1a) is an Sn₃S₄ semi-cube formed by three edge-sharing [SnS₅]⁶⁻ trigonal bipyramids. Six semi-cubes, oriented alternately up and down, define a 24-membered ring as shown in Fig. 1(b). The rings, approximately 8.3 Å in radius, bridge through semi-cubes forming Sn₃S₇ sheets similar to that found in TMA-SnS-1. The structure (Fig. 2) consists of sheets stacked parallel to (001).

Bond-valence sums (Brown & Wu, 1976) were consistent with oxidation states of +4 and -2 for Sn and S, respectively. Therefore, the Sn₃S₇ sheet is negatively charged with charge compensation being achieved by protonation of either the framework or the extra-framework organic species residing between the sheets.