Organic Chemistry

Synthesis and X-ray structural study of bis(2-sodiumsulfonylethyl) sulfoxide hexahydrate*

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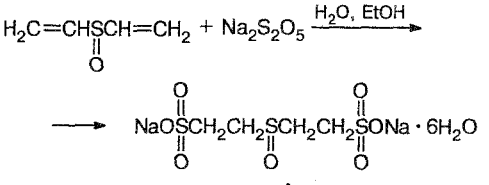
The structure of bis(2-sodiumsulfonylethyl) sulfoxide hexahydrate (**1**), which was synthesized by the reaction of divinyl sulfoxide with sodium metabisulfite in an aqueous ethanol medium, has been determined by X-ray structural analysis. Both Na^+ cations are coordinated by six O atoms of crystallization water molecules and SO_3 groups; the coordination sphere is a distorted octahedron. The crystals are stabilized by an extensive network of hydrogen bonds through the water molecules of crystallization.

Key words: divinyl sulfoxide; sodium metabisulfite; bis(2-sodiumsulfonylethyl) sulfoxide, X-ray structural study.

The reaction of divinyl sulfoxide with sodium metabisulfite has not been studied previously. However, it is known[1] that divinyl sulfoxide readily adds different nucleophiles, including amines, diamines, amino acids, amino alcohols, and their vinyl ethers. Many of the compounds obtained are characterized by a wide range of biological activities.[2]

Previously we pointed to the possibility of the synthesis of bis(2-sodiumsulfonylethyl) sulfoxide hydrate, which exhibits tranquilizing (anxiolytic)[3] and antiviral[4] activities as well as some technologically valuable properties.[5] In this work, we first demonstrated that sodium metabisulfite readily reacts with divinyl sulfoxide with the formation of mono- and/or diadducts, depending on conditions. The chosen conditions of the process made it possible to perform the targeted synthesis with the formation of diadduct **1** exclusively.

The reaction of sodium metabisulfite with divinyl sulfoxide (a molar ratio of reagents is 1 : 1) proceeds readily at 80—85 °C in an aqueous ethanol medium during 5 h and affords compound **1** in 90 % yield.



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* Dedicated to Academician of the RAS N. S. Zefirov (on his 60th birthday).

† Deceased in August, 1995.

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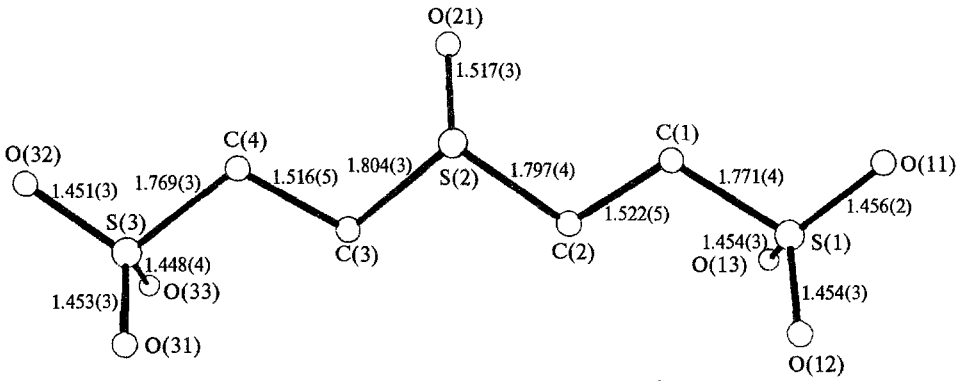

Fig. 1. Overall view of dianion **1** and bond lengths (Å) in the structure of **1**.

When the reaction is performed, the order, in which the reagents are mixed, is important: divinyl sulfoxide should be added to a solution of sodium metabisulfite.

Compound **1** is a crystalline white material that is readily soluble in water (soluble in DMSO upon heating), stable in storage, and nontoxic (LD_{50} = 3000 mg kg^{-1}).

The structure of bis(2-sodiumsulfonylethyl) sulfoxide hexahydrate **1** was established by X-ray structural analysis and confirmed by the results of ^1H and ^{13}C NMR, IR spectroscopy, and elemental analysis.

The crystal structure of **1** consists of $C_4H_8O_7S_3^{2-}$ dianions, the negative charges of which are located on the terminal SO_3 groups, two Na^+ cations, which are located near the charged ends of the dianion, and six molecules of crystallization water.

The overall view of the dianion and bond lengths are shown in Fig. 1; the bond angles are given in Table 1. The S(1)C(1)C(2)S(2)C(3)C(4)S(3) fragment is approximately planar (the deviations of the atoms from the mean plane are no more than ±0.224(4) Å). The S(2) atom has a pyramidal coordination and deviates from the plane passing through the C(2), O(21), and C(3) atoms by 0.704(1) Å; the S(1) and S(3) atoms have a tetrahedral coordination. The S(2)=O(21), S=O (SO_3), S—C, and C—C bond lengths are close to the normal values observed in analogous compounds.[6]

The crystal structure of **1** is typical of ionic crystals (Fig. 2). Both Na^+ ions are coordinated by six O atoms; however, the coordination spheres of these cations differ in composition: the $Na(1)^+$ cation is coordinated by two O atoms of two anions and four O atoms of H_2O molecules while the $Na(2)^+$ cation is coordinated by three O atoms of two anions and three O atoms of H_2O molecules. The Na—O distances are in the narrow range 2.337(4)—2.570(4) Å and fall within the range of values typical of organic ionic crystal hydrates[7—9] and Na-silicates.[10,11] The coordination polyhedra of both cations can be described as distorted octahedra. The distortion of coordination of Na^+ cations in the crystals of **1** is, apparently, determined by the concurrent participation of O atoms not only in ionic interaction but in formation of hydrogen bonds as well.

Table 1. Bond angles (ω) in anion **1**

Angle	ω/deg	Angle	ω/deg
O(11)—S(1)—O(12)	113.0(2)	O(31)—S(3)—O(33)	112.9(2)
O(11)—S(1)—O(13)	113.1(2)	O(31)—S(3)—C(4)	106.9(2)
O(11)—S(1)—C(1)	105.6(2)	O(32)—S(3)—O(33)	112.1(2)
O(12)—S(1)—O(13)	112.3(2)	O(32)—S(3)—C(4)	105.1(2)
O(12)—S(1)—C(1)	105.9(2)	O(33)—S(3)—C(4)	106.8(2)
O(13)—S(1)—C(1)	106.2(2)	S(1)—C(1)—C(2)	112.6(3)
O(21)—S(2)—C(2)	106.0(2)	S(2)—C(2)—C(1)	107.4(3)
O(21)—S(2)—C(3)	106.2(2)	S(2)—C(3)—C(4)	108.1(4)
C(2)—S(2)—C(3)	99.2(2)	S(3)—C(4)—C(3)	112.3(3)
O(31)—S(3)—O(32)	112.4(2)		

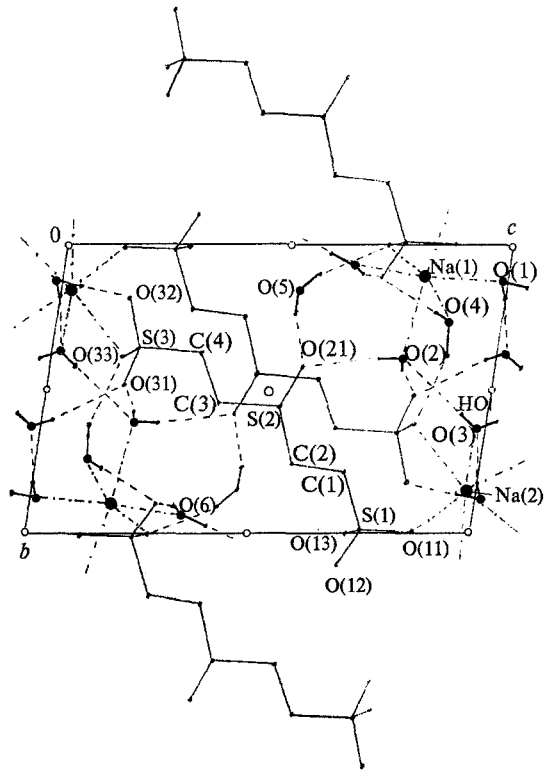

Fig. 2. The *bc* projection of the crystal structure of **1**. Hydrogen bonds are indicated by dashed lines; coordination of Na^+ cations is shown by dot-dash lines.

Table 2. Parameters of H—O—H...O hydrogen bonds in crystals of **1**

Bond	Symmetry operation*	O—H /Å	H...O /Å	O...O /Å	Angle O...H—O /deg
O(1)—HO(11)...O(32)	$x, y, z+1$	0.82(5)	2.00(5)	2.801(5)	164(5)
O(1)—HO(12)...O(3)	$-x, 1-y, 2-z$	0.72(6)	2.15(6)	2.858(4)	169(6)
O(2)—HO(21)...O(31)	$-x, 1-y, 1-z$	0.77(6)	2.07(5)	2.833(5)	172(5)
O(2)—HO(22)...O(21)	x, y, z	0.67(4)	2.30(4)	2.959(4)	171(5)
O(3)—HO(31)...O(31)	$x, y, 1+z$	0.62(6)	2.26(6)	2.868(4)	172(7)
O(3)—HO(32)...O(2)	x, y, z	0.57(6)	2.36(6)	2.932(4)	179(8)
O(4)—HO(41)...O(33)	$-x-1, 1-y, 1-z$	1.00(10)	2.10(9)	3.020(4)	152(9)
O(4)—HO(42)...O(12)	$x-1, y-1, z$	0.54(4)	2.34(4)	2.874(4)	173(6)
O(5)—HO(51)...O(13)	$x, y-1, z$	0.75(6)	2.11(6)	2.845(4)	164(7)
O(5)—HO(52)...O(21)	x, y, z	1.15(12)	1.81(11)	2.882(6)	153(8)
O(6)—HO(61)...O(5)	$x, 1+y, z$	0.77(6)	2.03(6)	2.768(5)	159(6)
O(6)—HO(62)...O(12)	$-x, 2-y, 1-z$	0.79(8)	2.12(8)	2.893(5)	166(7)

* For the donor O atoms derived from the basis atoms.

Table 3. Atomic coordinates ($\times 10^4$, $\times 10^3$ for H atoms) in the structure of **1**

Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
S(1)	−772(1)	9864(1)	7568(1)	Na(1)	−4191(2)	1056(2)	8153(1)	HC(41)	−227(6)	334(5)	356(3)
S(2)	−1852(1)	5560(1)	5312(1)	Na(2)	−2456(2)	8469(2)	9790(1)	HC(42)	−428(8)	282(8)	343(5)
S(3)	−3520(1)	3544(1)	1951(1)	O(1)*	−2474(3)	1225(3)	9858(2)	HO(11)	−270(6)	143(6)	1043(4)
O(11)	−280(3)	9924(3)	8715(2)	O(2)*	−2112(4)	3906(4)	7911(2)	HO(12)	−149(7)	177(7)	999(4)
O(12)	762(3)	11072(3)	7154(2)	O(3)*	−1368(4)	6303(4)	9808(2)	HO(21)	−106(6)	426(6)	795(4)
O(13)	−2483(3)	9981(3)	7221(2)	O(4)*	−5898(4)	2590(4)	8821(2)	HO(22)	−242(5)	389(5)	739(3)
O(21)	−3458(4)	4200(4)	5689(2)	O(5)*	−2430(6)	1548(5)	5361(3)	HO(31)	−138(8)	606(7)	1025(5)
O(31)	−1808(4)	4825(3)	1721(2)	O(6)*	−3788(5)	9308(5)	3466(3)	HO(32)	−152(8)	583(7)	944(5)
O(32)	−3915(5)	1828(2)	1562(2)	HC(11)	−220(7)	700(6)	725(4)	HO(41)	−568(13)	379(12)	891(8)
O(33)	−5106(4)	3839(4)	1602(2)	HC(12)	11(8)	791(8)	726(5)	HO(42)	−649(5)	227(5)	849(3)
C(1)	−1233(5)	7820(4)	6992(3)	HC(21)	−81(8)	829(8)	558(5)	HO(51)	−253(8)	97(7)	577(5)
C(2)	−1740(5)	7550(4)	5778(3)	HC(22)	−271(7)	757(7)	548(4)	HO(52)	−324(13)	232(12)	535(8)
C(3)	−2687(5)	5423(4)	3903(3)	HC(31)	−380(6)	555(5)	382(4)	HO(61)	−358(8)	973(7)	405(5)
C(4)	−3146(5)	3683(4)	3356(3)	HC(32)	−219(15)	610(14)	377(9)	HO(62)	−310(9)	903(8)	326(5)

* The O atoms of water molecules.

The extensive network of O —H...O hydrogen bonds observed in crystals of **1**, in which all active H atoms of water molecules are involved, is shown in Fig. 2. The lengths of the hydrogen bonds (Table 2) are within the range of normal values (see, for example, Ref. 12).

The role of water molecules is threefold. Firstly, lone electron pairs of O atoms are involved in interactions with Na^+ cations; secondly, these lone electron pairs act as acceptors of H atoms in hydrogen bonds with other water molecules; thirdly, H_2O molecules act as donors of H atoms in hydrogen bonds with O atoms of anions and other water molecules.

Experimental

The IR spectra were recorded on a Specord-75IR spectrophotometer in Vaseline oil or using KBr pellets for solids. The NMR spectra were obtained on a Tesla BS-567-A spectrometer (100 MHz for ^1H and 25.14 MHz for ^{13}C) in DMSO-d_6 with HMDS as an internal standard.

Bis(2-sodiumsulfonylethyl) sulfoxide hexahydrate (1). Ethanol (10 mL) was added to an aqueous solution (14 mL) of sodium metabisulfite (9.5 g), the reaction mixture was heated to 80—85 °C, then divinyl sulfoxide (5.1 g) was added to the solution, and the solution was stirred for 5 h. The crystals formed were filtered off, washed with ethanol, and dried at room temperature. The yield of **1** was 13 g (90 %), m.p. 120—123 °C (decomp. at 300 °C). Found (%): C, 11.97; H, 5.30; S, 23.06; Na, 11.17. $C_4H_8Na_2O_7S_3 \cdot 6H_2O$. Calculated (%): C, 11.50; H, 4.80; S, 23.00; Na, 11.00. IR, ν/cm^{-1}: 1028—1035 (S=O); 1120—1230 (SO_3Na); 1630—1660 (δHOH, H_2O (hydrate)); 3430—3530 br (OH, H_2O (hydrate)). ^1H NMR, δ: 2.84 (m, CH_2S=O, CH_2SO_3Na). ^{13}C NMR, δ: 44.08 (s, CH_2S=O); 47.37 (s, CH_2SO_3Na).

Crystals of $C_4H_8Na_2O_7S_3 \cdot 6H_2O$ (**1**) are triclinic, at 20 °C a = 8.2320(5) Å, b = 8.9242(5) Å, c = 12.8879(6) Å, α = 93.462(4)°, β = 99.923(5)°, γ = 116.862(4)°, V = 821.6(4) Å^3, d_{calc} = 1.691 g cm^{-3}, Z = 2, space group $P\bar{1}$. The unit-cell parameters and intensities of 4215 independent reflections were measured on an four-circle automated Hilger-Watts diffractometer (Mo-Kα radiation, graphite monochromator, $\theta/2\theta$ scanning technique up to θ_{max} = 30°). The structure was solved by the direct method using the MULTAN program and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms using 3809 reflections with $I > 2\sigma(I)$. The positions of the hydrogen atoms were located from the difference synthesis and refined isotropically.

The final R values are as follows: $R = 0.072$, $R_w = 0.077$. All calculations were carried out on an Eclipse S/200 computer using the INEXTL program package.[13] Atomic coordinates are given in Table 3 (thermal parameters for atoms may be obtained from the authors).

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