ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 5, pp. 969–971. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © R.E. Khoma, V.O. Gel'mbol'dt, O.V. Shishkin, V.N. Baumer, L.V. Koroeva, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 5, pp. 834–836.

Synthesis, Crystal Structure, and Spectral Characteristics of *N*-(Hydroxyethyl)aminomethanesulfonic Acid

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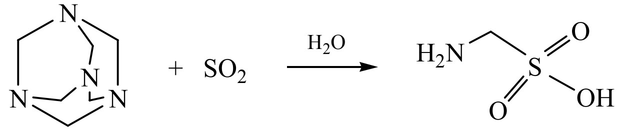
Received March 19, 2012

Abstract—A new method of the synthesis of *N*-(hydroxyethyl)aminomethanesulfonic acid by reaction in SO_2–$H_2NCH_2CH_2OH$–CH_2O–H_2O system was developed. Compound $HO(CH_2)_2NHCH_2SO_3H$ was characterized by XRD, IR and mass spectroscopy.

DOI: 10.1134/S1070363213050149

We have previously shown [1] that the interaction of sulfur(IV) oxide with hexamethylenetetramine (HMTA) in aqueous solution results in aminomethanesulfonic acid.



This method has several advantages over the previously published protocols of the synthesis of α-aminoalkanesulfonic acids, which are of interest due to various types of biological activity [2, 3]. Since this reaction can apparently include the acid-catalyzed hydrolysis of HMTA to form formaldehyde and ammonia, an attempt was made to synthesize derivatives of aminomethanesulfonic acid using formaldehyde and various amine components in the reaction. The present report describes the original synthesis and the results of studying the structure and spectral characteristics of *N*-(hydroxyethyl)aminomethanesulfonic acid $HO(CH_2)_2NHCH_2SO_3H$ as the product of reaction in the sulfur(IV) oxide – monoethanolamine–formaldehyde–water.

According to the XRD data, the compound obtained crystallizes in monoclinic system, space group $P2_1/c$, a 8.7863(7), b 5.3867(4), c 13.5574(10) Å; α 90, β 96.669(7), γ 90°; V 637.32(8) Å^3, T 293 K, Z 4, ρ 1.617 g cm^{-3}, F(000) 328, μ 0.453 mm^{-1} [λ(MoK_α) 0.71073 Å], ω-scanning at 3.60 ≤ θ ≤ 50.0°, 2135 measured reflections, of which 1112 are independent (R_{int} 0.015), final values of reliability indices of observed reflections are: R_F 0.0284, wR^2 0.0823 (R_F 0.0325, wR^2 0.0857 for all independent reflections), S 0.949.

Structure of *N*-(hydroxyethyl)aminomethanesulfonic acid molecule is shown in Fig. 1. The fragment O^1–S^1–C^1–N^1–C^2 is almost flat, torsion angles $C^2N^1C^1S^1$ and $O^1S^1C^1N^1$ are 175.70(10) and 178.11(10)°, respectively. The bending of the non-hydrogen atoms chain of the molecule can be characterized by the torsion angles $C^1N^1C^2C^3$ –67.85(17)° and $N^1C^2C^3O^4$ –57.09(17)°. When packed in the crystal, neighboring molecules are oriented by their sulfo-groups in opposite directions on the axis a, wherein the system of hydrogen bonds is formed as shown in Fig. 2 (see the table). Due to such hydrogen bonding in the structure the layers are formed in the crystallographic planes (100). Between the adjacent layers in the [100] direction there is no hydrogen bonding. Probably, this is the reason why the crystals have a plate habit and are very prone to twinning.

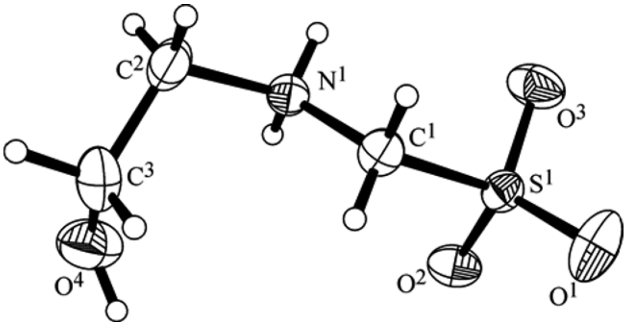


Fig. 1. General view of the molecule of *N*-(hydroxyethyl)aminomethanesulfonic acid (50% probability).

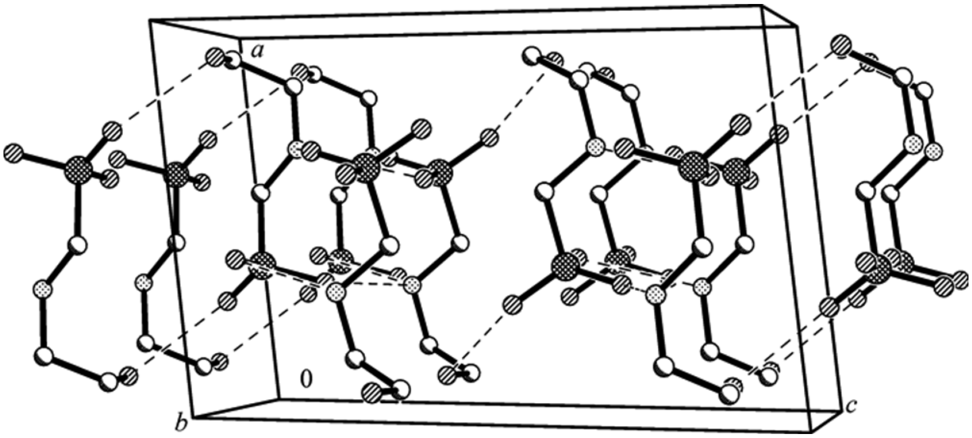


Fig. 2. The system of hydrogen bonding in the structure of *N*-(hydroxyethyl)aminomethanesulfonic acid (no hydrogen atoms are shown).

EXPERIMENTAL

The IR spectra were recorded on a Spectrum BX II FT-IR System spectrophotometer (Perkin-Elmer) in the region of 4000–350 cm^{-1} from KBr pellets. Mass spectra were taken on a MKh-1321 instrument (direct sample admission into the ion source, energy of ionizing electrons 70 eV).

Elemental analysis was carried out on a CHN elemental analyzer, and sulfur was determined by Schoeniger method. X-Ray analysis was performed on an Oxford Diffraction diffractometer (MoK_α-irradiation, graphite monochromator, CCD-detector Sapphire-3). The structure was solved and refined using the program package SHELX-97. [4] The hydrogen atoms were found from a difference synthesis and refined in an isotropic approximation. Atomic coordinates, geometric parameters of the molecule, and the crystallographic data are deposited in the Cambridge Structural Database (CCDC 865839).

***N*-(Hydroxyethyl)aminomethanesulfonic acid.** To a solution of 0.10 mol of monoethanolamine in 20 ml of water was added paraformaldehyde in an equimolar ratio when cooled to ≤ 10°C and kept for 24 h. Then through the resulting solution SO_2 was bubbled to pH ≤ 1.0 followed by keeping the reaction mixture at room

Hydrogen bonds D–H···A lengths and angles in the structure of *N*-(hydroxyethyl)aminomethanesulfonic acid

D–H···A	H···A, Å	DHA, deg	Symmetry operation
$O^4–H^4\cdots O^1$	1.97(2)	167(2)	$-x + 1, -y, -z + 2$
$N^1–H^{1A}\cdots O^2$	2.03(2)	172.6(18)	$-x + 1, y + 1/2, -z + 3/2$
$N^1–H^{1A}\cdots O^3$	2.623(18)	116.2(14)	$-x + 1, y + 1/2, -z + 3/2$
$N^1–H^{1B}\cdots O^3$	2.091(16)	151.0(17)	$-x + 1, y - 1/2, -z + 3/2$

temperature until complete evaporation of the water. Yield 15.5 g (100%), crystalline substance of light yellow color, mp 136–137°C. IR spectrum, ν, cm^{-1}: 3434 (OH), 3158, 3096 (NH), 3026, 2968, 2845 (NH, CH), 2694, 2367 (N^+H), 1233, 1201 (SO_2, ν_{as}), 1062, 1042 (SO_2, ν_s), 548 (S–O). As in the case of aminomethanesulfonic acid [1], the characteristics of the IR spectrum indicate the realization of the zwitterionic structure of *N*-(hydroxyethyl)aminomethanesulfonic acid. Mass spectrum (EI), *m*/*z* (I_{rel}, %): 86 (7), 72 (15), $[SO_2]^+$ 64 (100), 48 (42). Found, %: C 21.92; H 5.62; N 8.85; S 20.87. $C_3H_9NO_4S$. Calculated, %: C 23.22; H 5.85; N 9.03; S 20.66. *M* 155.17.

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