

LETTERS  
TO THE EDITOR

## Features of Interaction in the Sulfur(IV) Oxide–Hexamethylenetetramine–Water System: A First Example of Identification of the Product with a Sulfur–Carbon Bond

R. E. Khoma<sup>a,b</sup>, A. A. Shestaka<sup>a</sup>, O. V. Shishkin<sup>c</sup>, V. N. Baumer<sup>c</sup>,  
Yu. E. Brusilovskii<sup>d</sup>, L. V. Koroeva<sup>a</sup>, A. A. Ennan<sup>a</sup>, and V. O. Gel'mbol'd<sup>a,e</sup>

<sup>a</sup> Physicochemical Institute of Environmental and Human Protection, Ministry of Education and Science of Ukraine,  
National Academy of Sciences of Ukraine, ul. Preobrazhenskaya 3, Odessa, 65082 Ukraine  
e-mail: rek@onu.edu.ua, r\_khoma@farlep.net

<sup>b</sup> Mechnikov Odessa National University, Odessa, Ukraine

<sup>c</sup> Institute of Single Crystals, Kharkov, Ukraine

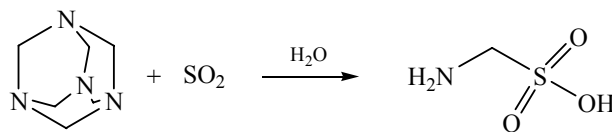
<sup>d</sup> Bogatskii Physicochemical Institute, Odessa, Ukraine

<sup>e</sup> Odessa State Medical University, Odessa, Ukraine

Received August 9, 2010

DOI: 10.1134/S1070363211030352

Hexamethylenetetramine (HMTA) is a ligand in the synthesis of coordination compounds and also is used as a pharmaceutical antiseptic drug and as hexogen precursor [1]. An attempt is known to use aqueous solutions of HMTA as an absorbent for extracting hydrogen fluoride and sulfur dioxide from the flue gases of aluminum production [2, 3]. In the study on the interaction in the HMTA–H<sub>2</sub>SO<sub>3</sub>–H<sub>2</sub>O system [4] a formation was found of compounds 2HMTA·H<sub>2</sub>SO<sub>3</sub>·6H<sub>2</sub>O and HMTA·2H<sub>2</sub>SO<sub>3</sub>·8H<sub>2</sub>O, the hexamethylenetetrammonium sulfite and bisulfite, respectively, hydrated forms. On the other hand, in acidic solutions HMTA is prone to hydrolysis to form ammonia and formaldehyde that does not exclude further deeper chemical reactions in the system HMTA–H<sub>2</sub>SO<sub>3</sub>–H<sub>2</sub>O (HMTA–SO<sub>2</sub>–H<sub>2</sub>O), as indicates indirectly the formation of H<sub>2</sub>NCH<sub>2</sub>SO<sub>3</sub>Na in the reaction of sodium hydrosulfite with formaldehyde and ammonia [5]. In this communication we report on the conditions of synthesis and the results of identification of a new compound, H<sub>2</sub>NCH<sub>2</sub>SO<sub>3</sub>H, aminomethanesulfonic acid, first isolated as a reaction product in HMTA–SO<sub>2</sub>–H<sub>2</sub>O system:



**Aminomethanesulfonic acid.** A solution of HMTA (5.0 g) in 30 ml of water was loaded to a reactor, cooled, and kept at 0°C for 20 min. Through this mixture gaseous SO<sub>2</sub> was bubbled at the rate 50 ml min<sup>–1</sup> to pH < 1.0. The amorphous precipitate formed which partly dissolved at further SO<sub>2</sub> passage. The solution with precipitate was kept at room temperature in air to complete water evaporation (~10 days). Yield 8.2 g (51.57% by N), white polycrystalline substance. The product was purified by recrystallization from water. Found, %: C 10.92; H 4.33; N 12.80; S 27.93. CH<sub>5</sub>NO<sub>3</sub>S. Calculated, %: C 10.81; H 4.54; N 12.60; S 28.86. *M* 111.1; mp 184°C (decomp.) (184°C [6]). IR spectrum, ν, cm<sup>–1</sup>: 3365, 3220, 3160, 3025 (N–H); 2982, 2908 (C–H); 2673, 2620, 2580, 2488, 2400, 1971 (N–H in hydrogen bond); 1230, 1207 (SO<sub>2</sub>, as), 1060, 1000 (SO<sub>2</sub>, s), 579 (S–O). The band ν(N–H) in the range of 3365–1970 cm<sup>–1</sup> is characteristic of NH<sub>3</sub><sup>+</sup>.

groups in the system of hydrogen bonds, which indicates the significant (preferential) contribution into the ground state of the molecules of zwitter-ionic structure. Raman spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3095, 3027 (N–H); 2880 (C–H); 1229, 1177 ( $\text{SO}_2$ , as), 1057, 1052 ( $\text{SO}_2$ , s), 581 (S–O). Mass spectrum (EI),  $m/z$  ( $I_{\text{rel}}$ , %): 64 (100), 48 (31), 42 (15). The mass spectrum of **I** is in accordance with the published data [7].

The IR spectra were recorded on a Spectrum BX II FT–IR System (Perkin-Elmer) instrument in the range of 4000–350  $\text{cm}^{-1}$  from KBr pellets. The Raman spectra were measured on a laser spectrometer DFS-24 with excitation from a semiconductor laser ( $\lambda$  532 nm; interference monochromator). The mass spectra (EI) were registered on a MX-1321 instrument (70 eV). The X-ray analysis was made on a Siemens D500 automated powder diffractometer at the copper radiation ( $\lambda$  1.5418 Å) with a graphite monochromator. Search in the database PDF-1 [8] showed that the lines in the diffraction pattern corresponded to amionomethanesulfonic acid  $\text{NH}_2\text{CH}_2\text{SO}_3\text{H}$ . By means of indexing of diffraction lines and its processing by the Rietveld method by FullProf program [9] in a mode of reference lines it was established that the substance belongs to the monoclinic system, space group  $Pn$ ,  $a$  5.19655(6),  $b$  7.27642(9),  $c$  5.15818(10) Å,  $\beta$  98.6785(9)°,  $V$  192.809(5) Å<sup>3</sup>,  $Z$  2.

## REFERENCES

1. *Obshchaya organicheskaya khimiya* (Comprehensive Organic Chemistry), Barton, D. and Ollis, W.D., Eds., Moscow: Khimiya, 1982, vol. 3, 736 p.
2. Brazovskaya, O.M., *Candidate Sci. (Chem.) Dissertation*, Odessa, 1979.
3. Ennan, A.A., Brazovskaya, O.M., Kosheleva, N.N., and Mikhailovina, S.K., USSR Inventor's Certificate no. 801860, 1978; *Byull. Izobret.*, 1981, no. 5.
4. Ennan, A.A., Brazovskaya, O.M., and Gryutstner, D., *Zh. Neorg. Khim.*, 1977, vol. 22, no. 6, p. 1679.
5. Long, R.D., Hiliard, N.P., Chhatre, S.A., Timofeeva, T.V., Yakovenko, A.A., Dei, D.K., and Mensahl, E.A., *Beilstein J. Org. Chem.*, 2010, vol. 6, no. 31, doi:10.3762/bjoc.6.31.
6. <http://www.sigmaaldrich.com>.
7. <http://webbook.nist.gov/cgi/cbook.cgi?ID=C13881919-&Units=SI&Mask=200#Mass-Spectra>. JCPDS PDF-1 File. International Committee for Diffraction Data, release 1994. PA, USA.
8. Rodriguez-Carvajal, J. and Roisnel, T., *FullProf.98 and WinPLOT: New Windows 95/NT Applications for Diffraction. Commission for Powder Diffraction, International Union of Crystallography*, Newsletter No. 20 (May-August) Summer 1998.