PHYSICAL METHODS
OF INVESTIGATION

Synthesis and Structure of Aminoguanidinium Sulfite Monohydrate

R. E. Khoma[a, b]**, V. O. Gelmboldt**[a, c]**, V. N. Baumer**[d]**, O. V. Shishkin**[d]**, and L. V. Koroeva**[a]

[a] *Physicochemical Institute for Human and Environment Protection, Ministry of Education and Science
and National Academy of Sciences of Ukraine, ul. Preobrazhenskaya 3, Odessa, 65026 Ukraine*
[b] *Mechnikov National University, ul. Dvoryanskaya 2, Odessa, 65025, Ukraine*
[c] *Odessa National Medical University, per. Valikhovskogo 2, Odessa, 65026 Ukraine*
[d] *Institute for Single Crystals, National Academy of Sciences of Ukraine, pr. Lenina 60, Kharkiv, 61178 Ukraine*
e-mails: rek@oni.edu.ua; r_khoma@farlep.net
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Abstract—The reaction between sulfur(IV) oxide and an aqueous suspension of aminoguanidinium hydrocarbonate yields $(CN_4H_7)_2SO_3 \cdot H_2O$, an "onium" sulfite, which has been characterized by X-ray diffraction and IR spectroscopy and mass spectrometry. The structure of the salt is stabilized by numerous H-bonds, such as NH···O, OH···O, and NH···N. The incorporation of pyramidal SO_3^{2-} ions into the network of H-bonds is accompanied by the lowering of their symmetry in comparison with C_{3v}, thus complicating the IR spectra of the salt in the region where the vibrations of the anion appear.

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Guanidine and its functional derivatives, in particular, aminoguanidine, are of interest due to their role in biochemical processes [1]. Aminoguanidine is also considered as a promising medicine for treating diabetic nephropathy [2]. As mono- or diacid base, aminoguanidine forms salts with mineral and organic acids, including structurally characterized nitrate [3], sulfate [4], hexafluorosilicate [5], dihydrophosphate [6], and hydrotartrate [7]. Aminoguanidinium nitrate finds application as a high-energy compound and a reagent in the synthesis of 5-aminotetrazole, which is the key product in technologies for the production of substituted high-energy tetrazoles [8, 9]. The aminoguanidinium salts [3, 6, 7] are also intensively studied in the context of searching for new materials for nonlinear optics [10]. Here, we describe a method for the synthesis of a new compound, aminoguanidinium sulfite monohydrate $(CN_4H_7)_2SO_3 \cdot H_2O$ (**I**), and the results of studying its structure and spectral characteristics.

EXPERIMENTAL

Synthesis of compound I. A suspension of aminoguanidinium hydrocarbonate (0.05 mol) in water (20 mL) is poured into a temperature-controlled cell and gaseous SO_2 was passed through it at a rate of 50 mL/min and a temperature of 0°C until pH < 1.0 was attained. The solution with a precipitate was allowed to stay at room temperature in air for water to evaporate. Separated colorless crystalline product **I**

(13.50 g; yield, 98.5%) was not subjected to any additional purification, and its $T_{melt} = 122-123°C$.

The nitrogen, carbon, and hydrogen were determined on an CHN elemental analyzer, and the sulfur was determined by the Schöniger method [11].

IR spectra were recorded on a Perkin-Elmer Spectrum BX II FT-IR System spectrometer (range: $4000-350$ cm^{-1}; KBr pellets), and mass spectra were taken on an MX-1321 mass spectrometer (direct injection; energy of ionizing electrons: 70 eV).

X-ray diffraction analysis was performed on an Oxford Diffraction diffractometer (MoK_α radiation, graphite monochromator, Sapphire-3 CCD detector). The structures were solved and refined using the SHELX-97 software suit [12]. Hydrogen atoms were found from a difference Fourier synthesis and refined in the isotropic approximation with overall thermal correction.

Selected crystallographic data and refinement details for the structure of compound **I** are the following: $C_2H_{16}N_8O_4S$, triclinic, FW = 248.29, space group P-1, $a = 5.4765(6)$ Å, $b = 14.3832(16)$ Å, $c = 14.8932(14)$ Å, $\alpha = 69.324(9)°$, $\beta = 89.459(8)°$, $\gamma = 88.633(9)°$, $V = 1097.3(2)$ Å^3 at $T = 293$ K, $Z = 4$, $\rho_{calcd} = 1.503$ g/cm^3, $F_{000} = 528$, crystal size $0.30 \times 0.15 \times 0.04$ mm, $\mu = 0.311$ mm^{-1} ($\lambda = 0.71073$ Å), transmittance coefficients $T_{min}/T_{max} = 0.912/0.988$; $-6 \le h \le 6$, $-15 \le k \le 17$, $-16 \le l \le 17$, ω-scanning at $3.72° \le \theta \le 50.0°$, 7153 measured reflections, of which 3663 reflections are independent ($R_{int} = 0.034$) and 3663 are observed reflections with $I_{hkl} > 2\sigma(I)$, coverage 98.5%, full-

Table 1. Bond lengths and bond angles in the structure of compound **I**

Bond	d, Å	Bond	d, Å
S(1)−O(1)	1.4993(12)	N(5)−N(6)	1.4143(18)
S(1)−O(3)	1.5065(10)	N(7)−C(2)	1.322(2)
S(1)−O(2)	1.5087(12)	N(8)−C(2)	1.3150(19)
S(2)−O(4)	1.4864(13)	N(9)−C(3)	1.322(2)
S(2)−O(6)	1.4975(13)	N(9)−N(10)	1.4114(18)
S(2)−O(5)	1.4978(10)	N(11)−C(3)	1.3126(18)
N(1)−C(1)	1.3194(17)	N(12)−C(3)	1.318(2)
N(1)−N(2)	1.4119(17)	N(13)−C(4)	1.334(2)
N(3)−C(1)	1.3303(19)	N(13)−N(14)	1.4122(18)
N(4)−C(1)	1.3123(19)	N(15)−C(4)	1.327(2)
N(5)−C(2)	1.3332(17)	N(16)−C(4)	1.3160(19)
Angle	ω, deg	Angle	ω, deg
O(1)S(1)O(3)	106.23(7)	N(4)C(1)N(3)	120.27(12)
O(1)S(1)O(2)	105.99(7)	N(1)C(1)N(3)	118.31(13)
O(3)S(1)O(2)	105.36(6)	N(8)C(2)N(7)	121.18(12)
O(4)S(2)O(6)	106.35(8)	N(8)C(2)N(5)	120.85(14)
O(4)S(2)O(5)	107.26(7)	N(7)C(2)N(5)	117.97(14)
O(6)S(2)O(5)	105.85(7)	N(11)C(3)N(12)	121.18(14)
C(1)N(1)N(2)	118.72(12)	N(11)C(3)N(9)	120.64(14)
C(2)N(5)N(6)	118.88(12)	N(12)C(3)N(9)	118.17(13)
C(3)N(9)N(10)	119.44(12)	N(16)C(4)N(15)	121.02(14)
C(4)N(13)N(14)	118.44(12)	N(16)C(4)N(13)	120.78(14)
N(4)C(1)N(1)	121.41(13)	N(15)C(4)N(13)	118.21(13)

matrix refinement of 193 parameters on F^2. The final values for the observed reflections: $R_F = 0.0417$, $wR^2 = 0.0979$ ($R_F = 0.0635$, $wR^2 = 0.1064$ for all independent reflections), GOOF = 0.980, $\Delta\rho_{min}/\Delta\rho_{max} = -0.213/0.460$ e/Å^3.

RESULTS AND DISCUSSION

The composition of compound **I** was established from elemental analysis.

For $C_2H_{16}N_8O_4S$, anal. calcd. (%): C, 9.68; N, 6.50; S, 12.92; H, 6.50.

Found (%): C, 9.91; N, 6.32; S, 12.52; H, 6.19.

Mass spectrum of compound **I**: [M]$^+$ ($m/z = 74$, $I = 94\%$); [SO$_2$]$^+$ ($m/z = 64$, $I = 74\%$); $m/z = 57$, $I = 23\%$; [SO]$^+$ ($m/z = 48$, $I = 25\%$); $m/z = 44$, $I = 19\%$; $m/z = 43$, $I = 64\%$; $m/z = 42$, $I = 14\%$; $m/z = 32$, $I = 100\%$.

The structure of compound **I** was proved by an X-ray diffraction study. Selected geometric characteristics and parameters of hydrogen bonds in the structure of compound **I** are listed in Tables 1 and 2, respectively.

The mutual arrangement of basis units is shown in Fig. 1. In all aminoguanidinium moieties, the terminal hydrazine nitrogen atoms are in pyramidal configuration, and a planar surrounding of the nitrogen atom is observed in the other NH and NH$_2$ groups. Each aminoguanidinium moiety is planar to within 0.02 Å. The sulfur atoms in sulfite ions have a pyramidal configuration.

In the crystal structure of compound **I**, there are numerous hydrogen bonds with the participation of aminoguanidinium groups, sulfite ions, and water molecules (Fig. 2). A three-dimensional framework in the crystal is formed due to H-bonds.

The results of analyzing the IR spectrum of compound **I** are displayed in Table 3. The assignment of aminoguanidinium ion vibrations is given in compliance with the data [6, 13]. A broad intense band in the IR spectrum with six sharply pronounced maxima in the region of 3420−2500 cm^{-1} is produced by the ν(OH) and ν(NH) vibrations of water molecules and the aminoguanidinium cation, respectively. The origin of a composite band with maxima at 2361, 2349, and

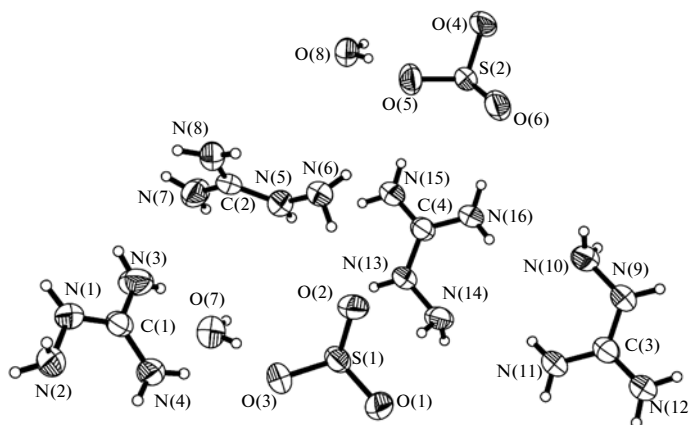**Fig. 1.** Numeration of the basis atoms and the ellipsoids of thermal vibrations in the structure of compound **I** (50-% probability).

Table 2. Characteristics of D−H···A hydrogen bonds in the structure of compound *I*

D−H···A contact	Distance, Å			DHA angle, deg	Atom A coordinates
	D−H	H···A	D···A		
O(7)−H(7D)···O(3)	0.793(7)	2.221(5)	2.9527(17)	153.6(9)	x, y, z
O(7)−H(7C)···O(3)	0.776(6)	2.121(4)	2.8589(17)	158.7(10)	$x − 1, y, z$
O(8)−H(8C)···O(6)	0.797(7)	2.342(9)	3.0784(17)	154.1(12)	$x − 1, y, z$
O(8)−H(8C)···O(5)	0.797(7)	2.368(6)	2.9948(16)	136.2(8)	$x − 1, y, z$
O(8)−H(8D)···O(5)	0.799(6)	1.983(6)	2.7719(16)	169.1(11)	x, y, z
N(1)−H(1)···O(4)	0.882(4)	1.903(5)	2.7842(17)	175.8(7)	$−x, −y + 1, −z + 1$
N(2)−H(2A)···O(7)	0.848(3)	2.261(4)	3.0694(17)	159.3(7)	$−x + 1, −y, −z + 1$
N(2)−H(2B)···O(4)	0.848(4)	2.515(4)	3.3376(19)	163.7(5)	$−x + 1, −y + 1, −z + 1$
N(3)−H(3A)···O(7)	0.819(3)	2.103(3)	2.8769(16)	157.5(9)	x, y, z
N(3)−H(3B)···O(5)	0.817(3)	2.383(5)	3.1656(19)	160.5(9)	$−x, −y + 1, −z + 1$
N(4)−H(4A)···O(3)	0.818(3)	2.229(4)	3.0059(14)	158.7(6)	x, y, z
N(4)−H(4B)···N(2)	0.817(3)	2.433(6)	3.1438(18)	146.1(8)	$−x + 2, −y, −z + 1$
N(5)−H(5)···O(2)	0.882(5)	2.031(5)	2.8480(17)	153.6(6)	$x − 1, y, z$
N(6)−H(6A)···O(2)	0.850(3)	2.119(4)	2.9576(17)	169.2(5)	x, y, z
N(6)−H(6B)···O(8)	0.851(3)	2.273(4)	3.0809(16)	158.5(8)	$x + 1, y, z$
N(7)−H(7A)···O(8)	0.817(3)	2.035(3)	2.8307(16)	164.6(10)	$−x − 1, −y + 1, −z + 1$
N(7)−H(7B)···O(2)	0.817(3)	2.499(5)	3.1483(15)	137.2(8)	$x − 1, y, z$
N(7)−H(7B)···O(3)	0.817(3)	2.596(6)	3.3628(19)	156.8(9)	$x − 1, y, z$
N(8)−H(8A)···O(5)	0.816(3)	2.234(4)	3.0163(15)	160.8(6)	$−x, −y + 1, −z + 1$
N(8)−H(8B)···N(6)	0.818(3)	2.462(7)	3.1627(19)	144.3(8)	$−x + 1, −y + 1, −z + 1$
N(9)−H(9)···O(6)	0.882(4)	1.960(5)	2.8359(17)	171.8(14)	$−x + 1, −y + 2, −z$
N(10)−H(10A)···O(4)	0.848(3)	2.625(4)	3.3899(17)	150.7(5)	$−x, −y + 2, −z$
N(11)−H(11A)···O(1)	0.816(3)	2.140(3)	2.9478(18)	170.5(4)	$−x + 2, −y + 1, −z$
N(11)−H(11B)···N(14)	0.818(3)	2.501(5)	3.2375(18)	150.4(6)	x, y, z
N(12)−H(12A)···O(4)	0.817(3)	1.973(3)	2.7906(16)	179.1(7)	$−x + 1, −y + 2, −z$
N(12)−H(12B)···O(3)	0.816(3)	2.093(4)	2.8986(18)	169.1(6)	$−x + 2, −y + 1, −z$
N(13)−H(13)···O(1)	0.881(5)	2.016(5)	2.8912(18)	172.7(15)	$x − 1, y, z$
N(14)−H(14B)···O(1)	0.848(4)	2.267(4)	3.0931(18)	164.8(7)	$−x + 1, −y + 1, −z$
N(15)−H(15A)···O(2)	0.819(3)	1.986(3)	2.7954(16)	169.8(7)	$x − 1, y, z$
N(15)−H(15B)···O(5)	0.817(3)	2.189(4)	2.9874(19)	165.4(6)	x, y, z
N(16)−H(16A)···O(6)	0.818(3)	2.117(3)	2.9253(19)	169.7(5)	x, y, z
N(16)−H(16B)···N(10)	0.816(3)	2.474(5)	3.1479(18)	140.7(6)	x, y, z

Table 3. Wavenumbers (cm^{-1}) of absorption band maxima in the IR spectrum of compound **I**

IR spectrum	Assignment
3420 sh	$\nu(NH)$, $\nu(OH)$
3402 s	
3300 s	
3167 m	
3020 sh	
2873 m	
2361 m	$\nu(OH\cdots OSO_2)$
2349 m	
2332 m	
1708 sh	$\delta(NH_2)$, $\delta(HOH)$
1671 s	
1461 m	$\delta(CNH)$, $\nu(CN)$
1420 w	
1383 w	
1250 sh	$\nu(NN)$, $\nu(CN)$, $\nu_s(CN_3)$, $\rho(NH_2)$, $\delta(CNH)$
1223 m	
1116 m	
1084 sh	$\nu_{as+s}(SO_3^{2-})$
1008 m	
931 s	
771 m	$\omega(NH_2)$, $\delta(CN_3)$
711 m	
672 sh	$\delta_s(SO_3^{2-})$, $\rho(NH_2)$, $\delta(NCN)$, $\delta(CNN)$, $\gamma(H_2O)$
666 sh	
620 m	
577 m	$\tau(NH_2)$, $\delta(CNH)$, $\delta(CN_3)$
506 sh	$\delta_d(SO_3^{2-})$
483 m	

Note: δ stands for scissoring, δ_d for out-of-plane, ω for wagging, τ for twisting, ρ for rocking, and γ for librational stretching vibrations.

2332 cm^{-1} may be explained by the presence of H-bonds like HOH$\cdots$OSO$_2$ in the structure of "onium" sulfite.

Within a range of 1750–1500 cm^{-1}, there is an intense band at 1671 cm^{-1} with a shoulder at 1708 cm^{-1}, which seems to belong to the overlapping scissoring bending vibrations of NH$_2$ and water typical for this region. In compliance with [6, 13], the bands at 1461, 1420, and 1383 cm^{-1} may be assigned to the mixed stretching and bending vibrations $\nu(CN)$ and $\delta(CNH)$.

According to [14], the vibrations of the pyramidal SO$_3^{2-}$ ion (idealized symmetry C_{3v}) are manifested in IR spectra as three characteristic groups of bands. The first group consists of symmetric and antisymmetric doubly degenerated vibrations $\nu_s(SO)$ (A_1) and $\nu_{as}(SO)$ (E) at 967 and 933 cm^{-1}, respectively. In the spectrum of compound **I**, an intense band with a maximum at 931 cm^{-1}, a medium intense band at 1008 cm^{-1}, and a shoulder at 1084 cm^{-1} should be assigned to these vibrations. There are no similar bands in the IR spectra of other aminoguanidinium salts, for example, in the chloride and hydrocarbonate spectra studied by us. The presence of the three absorption bands of $\nu(SO)$ in the IR spectrum of compound **I**, instead of two bands expected for the free SO$_3^{2-}$ ion, agrees with the X-ray diffraction data that the symmetry of the ion in cr4ystals of the complex lowers so that the split components of $\nu_{as}(SO)$ vibrations appear in the IR spectrum.

The second group consists of the band of symmetric bending vibrations $\delta_s(SO_3^{2-})$ (A_1) at 620 cm^{-1}. In the spectrum of compound **I**, the $\delta_s(SO_3^{2-})$ band is incorporated into a medium-intensity composite band in the region of 672–620 cm^{-1}, which includes the $\gamma(H_2O)$ librational vibration bands of water along with the bending vibration bands of the cation.

The third group is formed by the bands of the doubly degenerated out-of-plane vibrations $\delta_d(SO_3^{2-})$ (E) at 469 cm^{-1}. This vibration of the anion in the IR spectrum of compound **I** is represented by a medium-intensity band at 483 cm^{-1} with a shoulder at 506 cm^{-1}. A small splitting of this vibration ($\Delta\nu = 23$ cm^{-1}) reflects the slight distortion of the pyramidal geometry of the sulfite ion in the structure of compound **I**.

Hence, the reaction product in SO$_2$–H$_2$NC(=NH)NHNH$_2$–H$_2$O solutions is aminoguanidinium sulfite monohydrate (CN$_4$H$_7$)$_2$SO$_3 \cdot$ H$_2$O, whose structure has been established by X-ray diffraction . The structure of the "onium" sulfite is stabilized by a network of H-bonds. The involvement of the SO$_3^{2-}$ anion into interionic H-bonds lowers its symmetry with respect to C_{3v} and is accompanied by the complication of the IR spectrum of the complex in
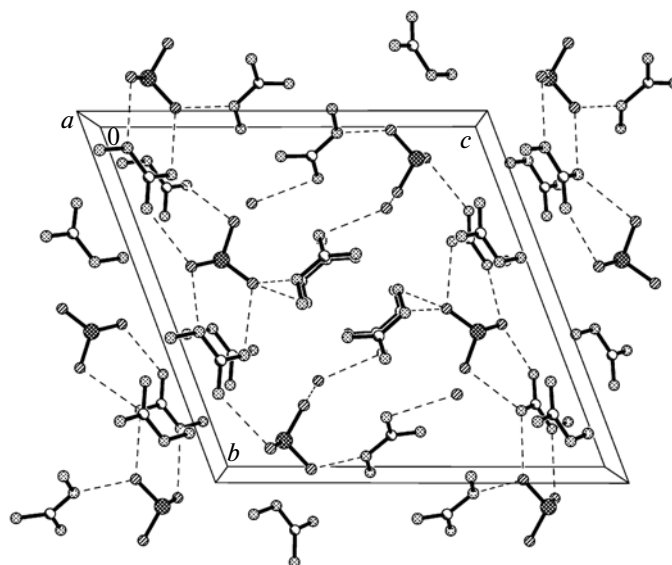
Fig. 2. Network of hydrogen bonds in the structure of compound **I** (hydrogen atoms are omitted).

the region of stretching and bending vibrations of the anion.

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