COORDINATION COMPOUNDS

Methylammonium Sulfate: Synthesis and Structure

R. E. Khoma[a, b], V. O. Gel'mbol'dt[c], V. N. Baumer[d, e], A. N. Puzan[d], and A. A. Ennan[a]

[a] Physicochemical Institute for Human and Environment Protection, Ministry of Education and Science of Ukraine, 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] Kharkiv National University, pl. Svobody 4, Kharkiv, 61077 Ukraine
e-mail: rek@onu.edu.ua
Received March 5, 2015

Abstract—The reaction between sulfur(IV) oxide and aqueous methylamine yields "onium" sulfate $(CH_3NH_3)_2SO_4$, which was characterized by X-ray diffraction, IR spectroscopy, and mass spectrometry. The structure of the sulfate is stabilized by a network of NH⋯O hydrogen bonds.

Methylamine (MA) is a reagent used in the synthesis of medicines, insecticides, fungicide, dyes, and rocket fuels [1]. The methylammonium cation forms salts with anions of various organic acids. Structurally characterized methylammonium compounds are chloride [2], dicitratoborate [3], bromide [4], trimolybdate hydrate [5], nitrate [6], perchlorate [7], and hexafluorosilicate [8]. Methylammonium sulfate is a commercial product (CAS 33689-83-7), though its crystal structure has not been yet studied. Vilminot et al. [9] only give crystallographic parameters for this compound assigned to space group $P2_1/c$.

Here we describe the results of structural and spectroscopicl characterization of methylammonium sulfate $(CH_3NH_3)_2SO_4$ isolated as a product of the reaction between sulfur(IV) oxide and aqueous MA in the presence of air oxygen.

EXPERIMENTAL

Synthesis of methylammonium sulfate (I). A temperature-controlled cell was poured with 40% aqueous MA (20 mL), through which gaseous SO_2 was passed at 0°C at a flow rate of 50 mL/min to adjust pH < 1.0. The resulting yellow oil-like product was allowed to stand at $T < 15°C$ in air until water evaporated. Separated colorless crystalline product **I** (15.43 g; yield, 83.4%) is converted into an ionic liquid at temperature above 20°C.

The nitrogen, carbon, and hydrogen were determined on an elemental CHN-analyzer, and the sulfur was estimated by the Schöniger method [10]. IR spectra were recorded on a Perkin Elmer Spectrum BX II FT-IR System spectrometer (range: 4000−650 cm^{-1}; samples in a BaF_2 liquid cell); electron-impact (EI) mass spectra were taken on an MX-1321 mass spectrometer (direct injection of a sample into the source; energy of ionizing electrons, 70 eV).

X-ray diffraction analysis was performed on an Oxford Diffraction Xcalibur 3 diffractometer (MoK_α, graphite monochromator, Sapphire-3 CCD detector). The structure was solved and refined using the SHELX-97 software suite [11]. 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: $C_2H_{12}N_2O_4S$, monoclinic, $M_r = 160.20$, space group $P 2_1/c$, $a = 13.1442(7)$ Å, $b = 8.8370(5)$ Å, $c = 13.5906(8)$ Å, $\beta = 113.154(7)°$, $V = 1451.46(14)$ Å^3 at $T = 293(2)$ K, $Z = 8$, $\rho = 1.466$ g/cm^3, $F_{000} = 688$, crystal of $0.40 \times 0.30 \times 0.2$ mm in size, $\mu = 0.403$ mm^{-1} ($\lambda(MoK_\alpha) = 0.71073$ Å), transmittance coefficients $T_{min}/T_{max} = 0.2953/0.9237$; $-12 \le h \le 17$, $11 \le k \le 11$, $-17 \le l \le 17$, ω-scans at $2.94° \le \theta \le 27.50°$, 6392 measured reflections, of which 3283 reflections are independent ($R_{int} = 0.0248$) and 2380 are observed with $I_{hkl} > 2\sigma(I)$; coverage, 98.6%; full-matrix refinement of 237 parameters on F^2: the final convergence values for the observed reflections $R_F = 0.0394$, $wR^2 = 0.1035$ ($R_F = 0.582$, $wR^2 = 0.1165$ for all independent reflections), $S = 0.941$, $\Delta\rho_{min}/\Delta\rho_{max} = -0.251/0.362$ e/Å^3.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent thermal corrections ($\text{Å}^2 \times 10^3$) in the structure of compound **I**

Atom	x/a	y/b	z/c	U_{eqv}
S(1)	10781(1)	2616(1)	4222(1)	34(1)
S(2)	5645(1)	2658(1)	4153(1)	38(1)
O(1)	11060(1)	1914(1)	5282(1)	47(1)
O(2)	11459(1)	1930(2)	3709(1)	58(1)
O(3)	11025(1)	4232(1)	4362(1)	60(1)
O(4)	9608(1)	2405(2)	3579(1)	63(1)
O(5)	4589(1)	1893(2)	3897(1)	63(1)
O(6)	6229(1)	2024(2)	3531(1)	62(1)
O(7)	5436(1)	4257(2)	3890(1)	79(1)
O(8)	6329(1)	2494(2)	5288(1)	65(1)
N(1)	11199(1)	4287(2)	6754(1)	43(1)
N(2)	8470(1)	1211(2)	4823(1)	44(1)
N(3)	6929(1)	−581(2)	1141(1)	45(1)
N(4)	5156(1)	1291(2)	6475(1)	50(1)
C(1)	12297(2)	4963(3)	7028(2)	61(1)
C(2)	8902(2)	1791(2)	5926(2)	53(1)
C(3)	7482(2)	29(3)	2208(2)	61(1)
C(4)	4018(2)	1873(3)	6083(2)	61(1)
H(1A)	11123(16)	3850(20)	7316(17)	72(1)
H(1B)	10685(16)	4990(20)	6499(16)	72(1)
H(1C)	11057(17)	3560(20)	6292(17)	72(1)
H(2A)	8859(17)	1650(20)	4496(16)	72(1)
H(2B)	7785(18)	1440(20)	4457(16)	72(1)
H(2C)	8556(17)	180(30)	4790(16)	72(1)
H(3A)	7365(18)	−1070(20)	983(17)	72(1)
H(3B)	6607(17)	130(30)	674(16)	72(1)
H(3C)	6433(17)	−1300(20)	1067(16)	72(1)
H(4A)	5487(18)	1680(20)	6118(17)	72(1)
H(4B)	5570(17)	1700(20)	7184(17)	72(1)
H(4C)	5193(16)	260(20)	6462(16)	72(1)
H(1D)	12362(17)	5300(20)	6398(17)	72(1)
H(1E)	12836(17)	4280(20)	7440(17)	72(1)
H(1F)	12397(17)	5700(30)	7451(17)	72(1)
H(2D)	8867(17)	2890(30)	5948(17)	72(1)
H(2E)	8445(18)	1470(30)	6198(17)	72(1)
H(2F)	9630(18)	1350(20)	6240(17)	72(1)
H(3D)	7951(17)	700(30)	2248(17)	72(1)
H(3E)	7748(17)	−720(30)	2693(17)	72(1)
H(3F)	6993(17)	460(20)	2422(16)	72(1)
H(4D)	4016(18)	2980(30)	6147(18)	72(1)
H(4E)	3689(18)	1550(20)	6499(17)	72(1)
H(4F)	3564(17)	1510(20)	5434(17)	72(1)

RESULTS AND DISCUSSION

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

For $C_2H_{12}N_2O_4S$ anal. calcd. (%): C, 15.00; N, 17.49; S, 20.03; H, 7.55.

Found (%): C, 14.81; N, 17.24; S, 19.73; H, 7.62.

EI mass spectrum of compound **I**: $[M + H]^+$ ($m/z = 32$, $I = 15\%$); $[M]^+$ ($m/z = 31$, $I = 75\%$); $[CH_2=NH_2]^+$ ($m/z = 30$, $I = 100\%$). The characteristic of MA fragmentation products in the mass spectrum of compound **I** and the tabular MA mass spectrum [12] are in good agreement. The mass spectrum of compound **I** shows the defragmentation [13] typical of 1-*n*-alkylamines with the formation of the $[CH_2=NH_2]^+$ ion, whose peak has a maximum intensity.

The structure of compound **I** was established by X-ray diffraction. The atomic coordinates and equivalent thermal corrections in the structure of compound **I** are listed in Table 1. The numbering of atoms and the ellipsoids of thermal vibrations in the independent cell part are shown in Fig. 1. Bond lengths and bond angles formed by non-hydrogen atoms in the structure are listed in Table 2. As can be seen from Fig. 1, the independent cell part contains four $CH_3NH_3^+$ cations and two SO_4^{2-} ions. The packing of these basic units in the crystal structure gives rise to hydrogen bonds, whose characteristics are given in Table 3. All the hydrogen atoms of ammonium groups participate in hydrogen bonds with the oxygen atoms of sulfate ions. Each ammonium group of the N_1, N_2, N_3, and N_4 atoms forms hydrogen bonds with the three closest sulfate ions, and one of the bonds formed by the ammonium group of the N_3 atom is forklike (Table 3). The network of hydrogen bonds observed in the structure of compound **I** is three-dimensional, as can be seen from Fig. 2.

The results of analyzing the IR spectrum of compound **I** are given in Table 4. The methylammonium vibrations were assigned using data from [14−18]. The broad band in the IR spectrum with three pronounced maxima in the region of 3380−3000 cm^{-1} is produced by the $\nu(NH_3^+)$ vibrations of the methylammonium cation. The complex band with maxima at 2597, 2506, 2360, and 2342 cm^{-1} seems to also arise from $\nu(NH_3^+)$ vibrations (3000−2000 cm^{-1}). The frequency range of 1600−1460 cm^{-1} features two intense bands at 1635 and 1521 cm^{-1}, which seem to belong to the scissoring vibrations of NH_3^+ typical for this region. The twisting vibrations of ammonium groups $\tau(NH_3^+)$ were identified in the form of low-intense bands at 1276 and 1239 cm^{-1}.
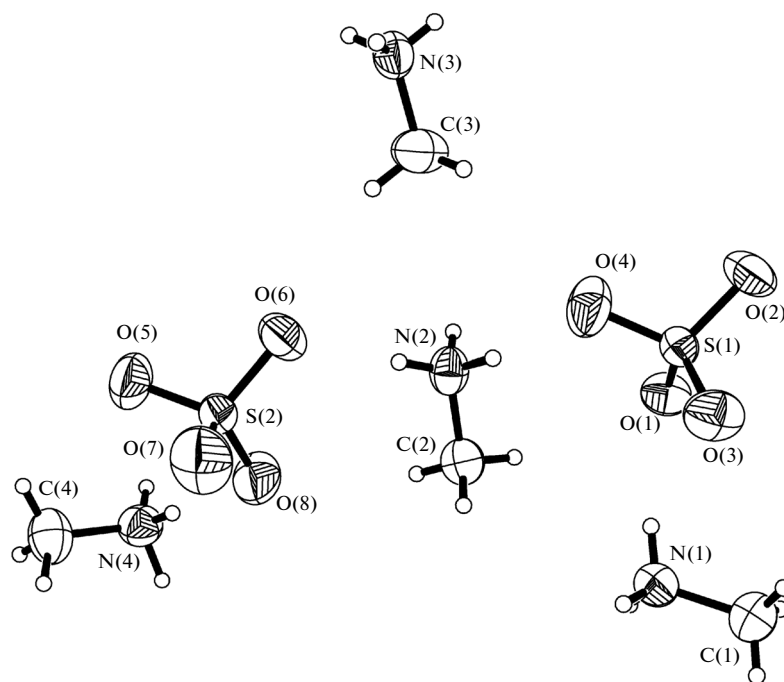
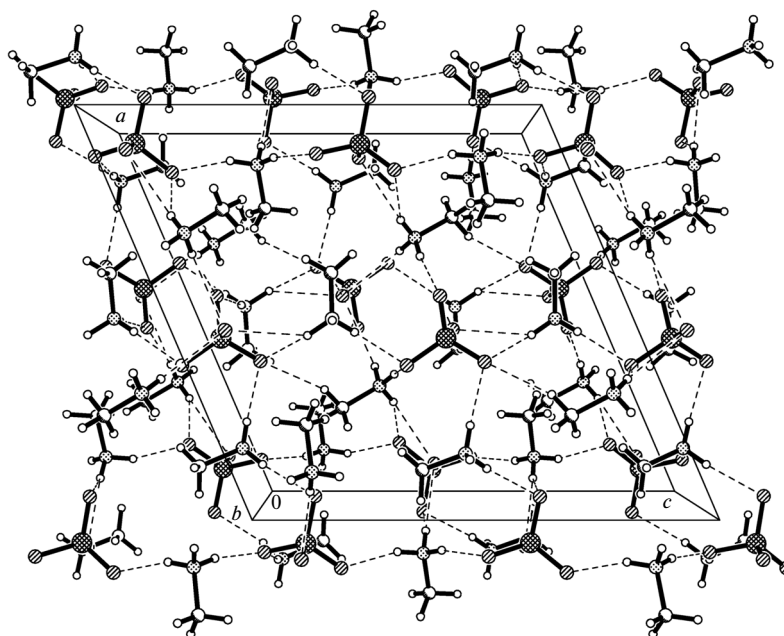**Fig. 1.** Numbering of atoms and the ellipsoids of thermal vibrations in the structure of compound **I** (50-% probability).

Fig. 2. Crystal packing and the network of hydrogen bonds (dashed lines) in the structure of compound **I**.

Stretching vibrations $\nu(N{-}CH_3)$ and scissoring vibrations $\delta(N{-}CH_3)$ appear at 2879, 2783 cm^{-1} and 1466, 1424 cm^{-1}, respectively.

The band at 969 cm^{-1} can be assigned to mixed straetching–bending vibrations $\nu_s(SO_4^{2-})$, $\tau(NH_3^+)$, and $\rho(CH_3)$. The bending vibrations $\delta_{as}(SO_4^{2-})$ are observed in the IR spectrum of compound **I** in its relatively "opened" part in the form of a high-intense band (at 668 cm^{-1}).

Hence, the reaction in $SO_2{-}CH_3NH_2{-}H_2O{-}O_2$ solutions produces methylammonium sulfate $(CH_3NH_3)_2SO_4$, whose three-dimensional structure is stabilized by a network of NH···O hydrogen bonds

Table 2. Bond lengths and bond angles in the structure of compound **I**

Bond	d, Å	Bond	d, Å	Bond	d, Å
S(1)–O(4)	1.4540(13)	S(2)–O(8)	1.4556(13)	N(1)–C(1)	1.469(2)
S(1)–O(3)	1.4601(13)	S(2)–O(7)	1.4569(15)	N(2)–C(2)	1.471(2)
S(1)–O(2)	1.4621(13)	S(2)–O(5)	1.4578(13)	N(3)–C(3)	1.448(3)
S(1)–O(1)	1.4755(11)	S(2)–O(6)	1.4585(13)	N(4)–C(4)	1.469(2)

Angle	ω, deg	Angle	ω, deg
O(4)S(1)O(3)	109.32(8)	O(8)S(2)O(7)	109.55(9)
O(4)S(1)O(2)	111.16(8)	O(8)S(2)O(5)	109.88(8)
O(3)S(1)O(2)	108.86(8)	O(7)S(2)O(5)	108.73(9)
O(4)S(1)O(1)	109.33(8)	O(8)S(2)O(6)	109.24(8)
O(3)S(1)O(1)	109.05(7)	O(7)S(2)O(6)	108.81(10)
O(2)S(1)O(1)	109.10(7)	O(5)S(2)O(6)	110.61(9)

Table 3. Parameters 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(D–H)	d(H···A)	d(D···A)		
N(1)–H(1A)···O(2)	0.90(2)	1.90(2)	2.7607(19)	161.4(18)	$x, -y + 1/2, z + 1/2$
N(4)–H(4B)···O(6)	0.97(2)	2.03(2)	2.986(2)	167.1(18)	$x, -y + 1/2, z + 1/2$
N(4)–H(4B)···O(7)	0.97(2)	2.54(2)	3.193(2)	124.7(16)	$x, -y + 1/2, z + 1/2$
N(1)–H(1B)···O(3)	0.88(2)	2.20(2)	3.0112(19)	153.6(19)	$-x + 2, -y + 1, -z + 1$
N(1)–H(1B)···O(4)	0.88(2)	2.33(2)	3.082(2)	143.2(17)	$-x + 2, -y + 1, -z + 1$
N(1)–H(1C)···O(1)	0.86(2)	2.00(2)	2.8538(19)	168(2)	
N(2)–H(2A)···O(4)	0.89(2)	1.98(2)	2.864(2)	170.8(19)	
N(2)–H(2B)···O(6)	0.86(2)	2.00(2)	2.8651(18)	176(2)	
N(2)–H(2C)···O(1)	0.92(2)	1.93(2)	2.8460(19)	171.8(19)	$-x + 2, -y, -z + 1$
N(3)–H(3A)···O(2)	0.81(2)	2.28(2)	3.005(2)	150(2)	$-x + 2, y - 1/2, -z + 1/2$
N(3)–H(3A)···O(3)	0.81(2)	2.36(2)	3.029(2)	141.1(19)	$-x + 2, y - 1/2, -z + 1/2$
N(3)–H(3B)···O(8)	0.87(2)	2.16(2)	2.948(2)	149.3(19)	$x, -y + 1/2, z - 1/2$
N(3)–H(3B)···O(7)	0.87(2)	2.37(2)	3.139(2)	147.6(19)	$x, -y + 1/2, z - 1/2$
N(4)–H(4A)···O(8)	0.84(2)	2.00(2)	2.840(2)	177(2)	
N(4)–H(4C)···O(5)	0.91(2)	2.01(2)	2.901(2)	164.1(19)	$-x + 1, -y, -z + 1$

Table 4. Wavenumbers (cm^{-1}) of absorption band maxima in the IR spectra of compound **I**

IR spectrum	Assignment*
3372 m	
3263 m	
3023 s	$\nu_{as,s}(NH_3^+)$
2879 s	$\nu_{as,s}(N-CH_3)$, $\nu(NH_3^+)$
2783 s	
2597 m	
2506 w	
2360 m	
2342 w	$\nu(NH_3^+)$
1635 s	$\delta_{as}(NH_3^+)$
1521 s	$\delta_s(NH_3^+)$
1466 s	$\delta_{as}(N-CH_3)$
1424 w	$\delta_s(N-CH_3)$
1276 w	$\tau(NH_3^+)$
1239 w	
1057 vs	$\nu_{as}(SO_4^{2-})$, $\nu(CN^+)$
969 s	$\nu_s(SO_4^{2-})$, $\rho(CH_3)$
668 s	$\delta_{as}(SO_4^{2-})$

* Deformation vibrations: δ stands for scissoring, τ for twisting, and ρ for rocking bending vibrations.

with the participation of all the hydrogen atoms of the "onium" cation.

REFERENCES

1. *The Chemical Encyclopedic Dictionary* (Sovetskaya Entsiklopediya, Moscow, 1983) [in Russian].
2. E. W. Hughes and W. N. Lipscomb, J. Am. Chem. Soc. **68**, 1970 (1946).
3. I. I. Zviedre and S. V. Belyakov, Russ. J. Inorg. Chem. **54**, 1390 (2009).
4. E. J. Gabe, Acta Crystallogr. **14**, 1296 (1961).
5. B. Włodarczyk-Gajda, A. Rafalska-Łasocha, and W. Łasocha, Powder Diffr. **22**, 241 (2007).
6. M. Mylrajan, T. K. K. Srinivasan, and G. Sreenivasamurthy, J. Cryst. Spectr. Res. **15**, 493 (1985).
7. P. F. Zanazzi, Acta Crystallogr., Sect. B **24**, 499 (1968).
8. B. D. Conley, B. C. Yearwood, S. Parkin, and D. A. Atwood, J. Fluorine Chem. **115**, 155 (2002).
9. S. Vilminot, L. Cot, C. Avinens, and M. Maurin, Mater. Res. Bull. **6**, 189 (1971).
10. V. A. Klimova, *Selected Methods of Organic Analysis* (Khimiya, Moscow, 1975) [in Russian].
11. G. M. Sheldrick, Acta Crystallogr., Sect. A **64**, 112 (2008).
12. http://webbook.nist.gov/cgi/cbook.cgi?ID=C74895&Units=SI&Mask=200#Mass-Spec.
13. N. S. Vul'fson, V. G. Zaikin, and A. I. Mikaya, *Mass Spectrometry of Organic Compounds* (Khimiya, Moscow, 1986) [in Russian].
14. S. J. Baek, K.-W. Choi, Y. S. Choi, and S. K. Kim, J. Chem. Phys. **118**, 11040 (2003).
15. S. Grossman and N. D. Danielson, J. Chromatogr., A **1216**, 3578 (2009).
16. E. Pretsch, F. Buehlmann, and C. Affolter, *Structure Determination of Organic Compounds: Tables of Spectral Data* (Springer, Berlin, 2000; Mir, Moscow; BINOM, Laboratoriya Znanii, 2006).
17. B. N. Tarasevich, *IR Spectra of Major Classes of Organic Compounds. Reference Materials* (MGU, Moscow, 2012) [in Russian].
18. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (Interscience, New York, 1986).

Translated by E. Glushachenkova