

Products of Interaction between Sulfur(IV) Oxide and Aqueous Solutions of Hexamethylenediamine and *tert*-Butylamine: The Crystal Structure of Hexamethylenediammonium Sulfate Dihydrate

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Abstract—The possibility of mild SO₂ oxidation in sulfur(IV) oxide–alkylamine–water–oxygen systems is demonstrated to yield onium sulfates.

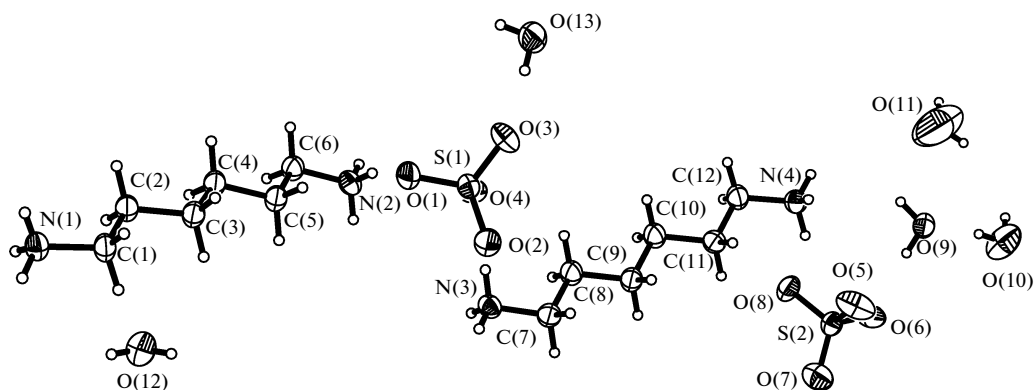
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The reaction between sulfur(IV) oxide and aliphatic mono- and diamines (L) in a gas phase and in aprotic solvents was shown to yield complexes of composition $n\text{SO}_2 \cdot \text{L}$ ($n = 1, 2$), whereas the same reaction in water yields onium sulfates $(\text{LH})_2\text{SO}_3$ and $(\text{LH}_2)\text{SO}_3$ [1–3]. We found that bubbling sulfur(IV) oxide into aqueous solutions of hexamethylenediamine (HMDA) and *tert*-butylamine (*tert*-BA), followed by exposure of the products in air, yields onium sulfates. Synthesis conditions and X-ray diffraction data for compounds $(\text{MDAH}_2)\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (**I**) and $(\text{tert-BAH})_2\text{SO}_4$ (**II**) are reported here.

EXPERIMENTAL

Synthesis of Hexamethylenediammonium Sulfate Dihydrate (**I**)

A temperature-controlled cell was filled with HMDA solution (0.043 mol) in 10 mL of water; gaseous SO₂ was bubbled into the solution at 0°C for ~1 h at a rate of 50 mL/min. The precipitate-containing solution was kept in air at room temperature until water was evaporated. The isolated white product (**I**) (10.35 g, yield 96.1% based on HMDA) was purified by recrystallization from water.



Crystal structure of compound **I** and thermal vibration ellipsoids (a 60% probability level).

Table 1. Atomic coordinates ($\times 10^4$) for non-hydrogen atoms and equivalent thermal corrections ($\text{\AA}^2 \times 10^3$) in structure **I**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
S(1)	2290(1)	1572(1)	2585(1)	24(1)
O(1)	2893(1)	1507(1)	2775(1)	35(1)
O(2)	2234(1)	1917(1)	3288(1)	31(1)
O(3)	2014(1)	419(1)	2281(1)	36(1)
O(4)	2018(1)	2502(1)	1977(1)	31(1)
S(2)	-2406(1)	5536(1)	289(1)	27(1)
O(5)	-2366(1)	4326(1)	615(1)	49(1)
O(6)	-3010(1)	5735(1)	-271(1)	42(1)
O(7)	-2219(1)	6396(1)	887(1)	47(1)
O(8)	-2088(1)	5536(1)	-178(1)	60(1)
O(9)	-3477(1)	3661(1)	-1064(1)	33(1)
O(10)	-4638(1)	4251(1)	-1713(1)	65(1)
O(11)	-4361(1)	3597(2)	-3447(1)	162(3)
O(12)	5348(1)	5559(1)	4722(1)	50(1)
O(13)	1502(1)	-416(1)	750(1)	45(1)
N(1)	6562(1)	2520(1)	5357(1)	27(1)
N(2)	3042(1)	3531(1)	1822(1)	27(1)
N(3)	1807(1)	4443(1)	2764(1)	26(1)
N(4)	-1800(1)	3028(1)	-233(1)	28(1)
C(1)	5941(1)	2432(1)	5090(1)	28(1)
C(2)	5604(1)	2560(1)	4211(1)	26(1)
C(3)	4971(1)	2557(1)	3966(1)	27(1)
C(4)	4610(1)	2836(1)	3102(1)	27(1)
C(5)	3992(1)	3040(1)	2894(1)	26(1)
C(6)	3647(1)	3308(1)	2031(1)	27(1)
C(7)	1209(1)	4398(1)	2621(1)	28(1)
C(8)	801(1)	4266(1)	1757(1)	29(1)
C(9)	189(1)	4145(1)	1611(1)	29(1)
C(10)	-226(1)	3884(1)	759(1)	30(1)
C(11)	-828(1)	3695(1)	647(1)	28(1)
C(12)	-1238(1)	3341(1)	-183(1)	31(1)

For $\text{C}_6\text{H}_{22}\text{N}_2\text{O}_6\text{S}$ anal. calcd. (%): C, 28.79; N, 11.19; S, 12.81; H, 8.86.

Found (%): C, 28.91; N, 11.33; S, 12.92; H, 8.95.

X-ray diffraction analysis. For crystals of **I**: $\text{C}_6\text{H}_{22.20}\text{N}_2\text{O}_{6.10}\text{S}$, monoclinic, FW = 252.12, space group $C2/c$, $a = 26.286(3)$ \AA, $b = 11.3980(8)$ \AA, $c = 19.2641(19)$ \AA, $\beta = 117.177(13)^\circ$, $V = 5134.5(8)$ \AA³ at $T = 105$ K, $Z = 16$, $\rho = 1.305$ g/cm³, $F_{000} = 2192$, crystal size $0.4 \times 0.3 \times 0.1$ mm, $\mu = 0.266$ mm⁻¹ ($\lambda(\text{MoK}\alpha) = 0.71073$ \AA), transmission coefficients $T_{\min}/T_{\max} = 0.901/0.974$; $-22 \leq h \leq 36$, $-10 \leq k \leq 15$, $-27 \leq l \leq 23$, ω scans at $3.16 \leq \theta \leq 30.0^\circ$, 14 100 reflections measured, of which 7389 are independent reflections ($R_{\text{int}} = 0.023$) and 5624 are observed reflections with $I_{hkl} > 2\sigma(I)$; coverage degree of 98.8; full-matrix refinement of 247 parameters with respect to F^2 where the final values for the observed reflections are $R_F = 0.0476$, $wR = 0.1398$ ($R_F = 0.0658$, $wR^2 = 0.1587$ for all independent reflections), $S = 0.936$, $\Delta\rho_{\min}/\Delta\rho_{\max} = -0.699/0.658$ e/\AA³. Atomic coordinates, selected geometric parameters, and parameters for hydrogen bonding (HB) in the structure of **I** are shown in Tables 1, 2, and 3, respectively.

The X-ray diffraction experiment was carried out on an Oxford Diffraction diffractometer (MoK α radiation, graphite monochromator, Sapphire-3CDD detector). Structures were solved and refined using the SHELX-97 program package [4]. Hydrogen atoms were determined from difference synthesis and refined using the rider model in methylene groups and in the isotropic approximation in ammonium groups and water molecules.

Synthesis of *tert*-Butylammonium Sulfate (**II**)

A white crystalline product (**II**) was prepared using the same sequence of operations for aqueous solution with *tert*-BA (0.068 mol of amine in 35 mL of H₂O) (isolated 8.32 g, yield 99.7% based on *tert*-BA).

For $\text{C}_8\text{H}_{24}\text{N}_2\text{O}_4\text{S}$ anal. calcd. (%): C, 39.32; N, 11.46; S, 13.12; H, 9.90.

Found (%): C, 40.21; N, 11.52; S, 12.93; H, 9.72.

Nitrogen, carbon, and hydrogen were determined using a CHN elemental analyzer; sulfur was determined using the Scheniger procedure [5, 6].

RESULTS AND DISCUSSION

The figure shows the structure of the symmetrically independent part of a unit cell of crystal **I**.

Hexamethylenediammonium cations have chain-like structure. Cationic chains in the structure are stretched along the [101] direction. Sulfate ions and

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

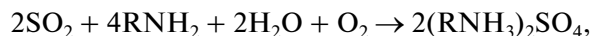
Bond	<i>d</i> , Å	Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
S(1)–O(1)	1.4562(9)	N(1)–C(1)	1.4738(13)	C(4)–C(5)	1.5050(14)
S(1)–O(2)	1.4828(9)	N(2)–C(6)	1.4747(14)	C(5)–C(6)	1.5156(13)
S(1)–O(3)	1.4866(8)	N(3)–C(7)	1.4690(14)	C(7)–C(8)	1.5199(14)
S(1)–O(4)	1.4964(7)	N(4)–C(12)	1.4796(15)	C(8)–C(9)	1.5084(15)
S(2)–O(7)	1.4186(10)	C(1)–C(2)	1.5173(13)	C(9)–C(10)	1.5285(14)
S(2)–O(6)	1.4737(9)	C(2)–C(3)	1.5101(14)	C(10)–C(11)	1.5112(16)
S(2)–O(8)	1.4838(11)	C(3)–C(4)	1.5262(13)	C(11)–C(12)	1.5190(14)
S(2)–O(5)	1.4989(9)				

Angle	ω, deg	Angle	ω, deg
O(1)S(1)O(2)	109.64(5)	N(1)C(1)C(2)	111.84(9)
O(1)S(1)O(3)	109.56(5)	C(3)C(2)C(1)	110.31(9)
O(2)S(1)O(3)	110.96(5)	C(2)C(3)C(4)	112.74(9)
O(1)S(1)O(4)	108.08(5)	C(5)C(4)C(3)	112.29(9)
O(2)S(1)O(4)	108.34(5)	C(4)C(5)C(6)	110.78(9)
O(3)S(1)O(4)	110.20(4)	N(2)C(6)C(5)	111.38(9)
O(7)S(2)O(6)	110.25(6)	N(3)C(7)C(8)	111.63(9)
O(7)S(2)O(8)	114.25(6)	C(9)C(8)C(7)	111.85(10)
O(6)S(2)O(8)	105.87(6)	C(8)C(9)C(10)	113.19(10)
O(7)S(2)O(5)	111.37(6)	C(11)C(10)C(9)	111.53(10)
O(6)S(2)O(5)	107.10(6)	C(10)C(11)C(12)	112.49(10)
O(8)S(2)O(5)	107.61(6)	N(4)C(12)C(11)	109.93(10)

water molecules bound to them via hydrogen bonds are located near the plane $x = 0.25$ in the cell unit. Cationic chains form a branched network of hydrogen bonds predominantly with sulfate ions (Table 3). Water molecules that are not bound to cations and anions via the hydrogen bonds reside within voids between the cationic chains (O(10), O(11), O(12) atoms); the O(11) positions of water molecules are only 20% filled.

According to the X-ray diffraction data, compound **II** is *tert*-butylammonium sulfate, which was structurally characterized [6].

Thus, the reactions in the systems under study can be described by the following scheme:



where the redox conversion is apparently due to exposure of the reaction products to an unprotected atmosphere.

Table 3. Characteristics of D–H...A hydrogen bonds in structure I

D–H...A contact	Distance, Å			DHA angle, deg	Coordinates of atom A
	D–H	H...A	D...A		
O(9)–H(9C)...O(6)	0.86	1.92	2.7778(10)	176	x, y, z
O(9)–H(9D)...O(2)	0.86	1.90	2.7579(11)	176	$x - 1/2, -y + 1/2, z - 1/2$
O(10)–H(10D)...O(10)	0.86	1.92	2.7453(11)	160	$-x - 1, y, -z - 1/2$
O(10)–H(10C)...O(9)	0.86	1.95	2.8018(8)	171	x, y, z
O(11)–H(11C)...O(12)	0.86	2.30	2.8066(12)	118	$-x, -y + 1, -z$
O(11)–H(11D)...O(10)	0.86	2.03	2.8847(12)	174	$-x - 1, y, -z - 1/2$
O(12)–H(12C)...O(13)	0.86	1.94	2.7693(8)	161	$x + 1/2, -y + 1/2, z + 1/2$
O(12)–H(12D)...O(12)	0.86	1.95	2.8103(15)	175	$-x + 1, -y + 1, -z + 1$
O(13)–H(13A)...O(3)	0.86	1.94	2.7910(10)	168	x, y, z
O(13)–H(13B)...O(6)	0.86	2.32	3.0891(13)	149	$x + 1/2, y - 1/2, z$
O(13)–H(13B)...O(5)	0.86	2.34	3.1166(15)	150	$x + 1/2, y - 1/2, z$
N(1)–H(1C)...O(8)	0.86	1.90	2.7510(14)	171	$-x + 1/2, y - 1/2, -z + 1/2$
N(1)–H(1D)...O(4)	0.92	1.89	2.7867(12)	165	$x + 1/2, -y + 1/2, z + 1/2$
N(1)–H(1E)...O(6)	0.96	1.87	2.8148(14)	172	$x + 1, -y + 1, z + 1/2$
N(1)–H(1E)...O(7)	0.96	2.62	3.1366(14)	114	$x + 1, -y + 1, z + 1/2$
N(2)–H(2C)...O(3)	0.90	1.91	2.8055(13)	175	$-x + 1/2, y + 1/2, -z + 1/2$
N(2)–H(2D)...O(1)	0.89	2.25	3.0816(13)	157	x, y, z
N(2)–H(2D)...O(4)	0.89	2.43	3.0732(13)	129	x, y, z
N(2)–H(2E)...O(6)	0.92	2.32	3.0667(14)	138	$-x, -y + 1, -z$
N(2)–H(2E)...O(8)	0.92	2.34	3.1927(14)	155	$-x, -y + 1, -z$
N(3)–H(3C)...O(4)	0.92	1.96	2.8746(12)	177	x, y, z
N(3)–H(3C)...O(2)	0.92	2.55	3.0878(12)	118	x, y, z
N(3)–H(3D)...O(5)	0.87	1.93	2.7830(13)	168	$-x, y, -z + 1/2$
N(3)–H(3E)...O(1)	0.88	1.95	2.8237(13)	173	$-x + 1/2, y + 1/2, -z + 1/2$
N(4)–H(4C)...O(2)	0.95	1.95	2.8212(12)	150	$x - 1/2, -y + 1/2, z - 1/2$
N(4)–H(4D)...O(8)	0.95	2.15	2.9706(14)	143	x, y, z
N(4)–H(4D)...O(5)	0.95	2.19	3.0473(16)	150	x, y, z
N(4)–H(4E)...O(9)	0.93	2.06	2.9699(11)	167	$-x - 1/2, -y + 1/2, -z$

Summarizing, let us note that the results described above are the first structurally confirmed example of mild oxidation of SO₂ into onium sulfates in the sulfur(IV) oxide–hexamethylenediamine (*tert*-butylamine)–water–O₂ systems.

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