Ammonium salts of sulfur-containing oxyanions resulting from reaction of sulfur dioxide with aqueous solutions of diethylentriamine and bis(hexamethylene)triamine

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AMMONIUM SALTS OF SULFUR-CONTAINING OXYANIONS RESULTING FROM REACTION OF SULFUR DIOXIDE WITH AQUEOUS SOLUTIONS OF DIETHYLENTRIAMINE AND BIS(HEXAMETHYLENE)TRIAMINE

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Interaction in the system «sulfur dioxide−diethylenetriamine (or bis-(hexamethylene)triamine)−water−air oxygen» results in a mixture of double salts (diethylenetriammonium bis(sulfito)-dithionate (Ia) and bis(sulfito)-sulfate trihydrate diethylenetriammonium (Ib)) or bis(hexamethylene)triammonium sulfate (II). The obtained ammonium salts of sulfur-containing oxyanions Ia, Ib, and II were characterized by the methods of elemental analysis, X-ray structural analysis, X-ray powder diffraction, IR spectroscopy, and mass spectrometry. Compound Ia crystallizes in monoclinic syngony (space group C2/c, a=28.1583(5) Å, b=6.84450(10) Å, c=10.8351(2) Å, β=93.776(2)^0, V=2083.71(6) Å^3, Z=4). Compound Ib crystallizes in rhombic syngony (space group Pbcn, a=18.9777(13) Å, b=10.3131(8) Å, c=11.5414(10) Å, V=2258.9(3) Å^3, Z=4). Compound II crystallizes in triclinic syngony (space group P-1, a=11.347(3) Å, b=11.700(5) Å, c=18.913(4) Å, α=95.22(3)^0, β=92,52(2)^0, γ=118,27(4)^0, V=2191,36 Å^3, Z=2). The IR spectrum of the mixture of salts Ia and Ib shows the valence vibrations of $\nu(SO)$ of sulfite anion (ν_1 and ν_3), represented by bands at 955, 931, 907, 1026, and 1006 cm^{-1}. Two bands at 566 and 493 cm^{-1} are the result of the splitting of a doubly degenerate out-of-plane deformation vibration of the ν_4 (E) of dithionate anion. The bands at 1127 and 1078 cm^{-1} correspond to the oscillations of ν_{as} and ν_s of sulfate anion (SO_4^{2-}). A decrease in the symmetry of the SO_4^{2-} anion as a result of salt formation is accompanied by the appearance of the band ν_1 (A_1) at 980 cm^{-1} in its spectrum.

Keywords: sulfur dioxide, 2-hydroxypropylamine, bis(hexamethylene)triamine, sulfoxidation, spectral characteristics.

Introduction

As is known, sulfur dioxide is one of the main atmospheric pollutants of anthropogenic origin (more than 200 million tons/year): the large-scale emission of this toxicant is accompanied by various negative effects on environmental objects, flora and fauna [1]. Therefore, efforts directed at the development of means for cleaning process gases, sanitary air purification from sulfur dioxide, especially with the use of chemisorption processes by aqueous solutions of organic chemisorbents based on amines and their derivatives are urgent. At the same time, polyamines, for example, triamines, can be considered as convenient models of polymeric (oligomeric) chemosorbents of the polyethylene polyamine type, on which it is possible to trace the features of chemical transformations in the specified chemisorption systems, namely, salt formation and sulfoxidation reactions. We chose diethylenetriamine (DETA) and bis(hexamethylene)triamine (BHMT) as model

triamines in this work.

DETA forms ammonium salts (mono-, di-, and triprotonated DETA cations) of the corresponding anions with mineral acids (HCl, HBr, HI, HNO$_3$, H$_2$SO$_4$, H$_3$PO$_4$, etc. [2]). Under the conditions of isothermal evaporation of the N(CH$_2$CH$_2$NH$_2$)$_2$−H$_2$SO$_4$−H$_2$O system, a mixed sulfate-hydrosulfate salt [DETAH$_3$]SO$_4$(HSO$_4$) is formed, similar to the AlkNH$_2$−SO$_2$−H$_2$O−O$_2$ systems (Alk=n-C$_7$H$_{15}$ and n-C$_8$H$_{17}$)−(AlkNH$_3$)$_3$SO$_4$(HSO$_4$) [3]. As a result of the interaction of monoprotonated DETA monobromide salt ([DETAH]Br) with sulfur dioxide, a mixed sulfite-hydrobromide salt of triprotonated DETA is formed: [DETAH$_3$](SO$_3$)Br [5]. The reaction of DETA with SO$_2$ in tetradecyl(trihexyl)phosphonium chloride in the presence of air oxygen is accompanied by the formation of a mixed sulfite-chloride salt [DETAH$_3$](SO$_3$)Cl, while in the presence of N-methylpyrrolidone and 95% ethanol, sulfite monohydrate [DETAH$_2$](SO$_3$)·H$_2$O is formed with protonated terminal N atoms [6,7].

From an aqueous solution of BHMT with orthophosphoric acid, triammonium hydrogen phosphate BHMT crystallizes in the form of undecahydrate [2]. There is a known case of the monoammonium cation

$$NH_2(CH_2)_6 \overset{+}{N} H_2 (CH_2)_6 NH_2$$

formation in the composition of a polynuclear platinum complex [8].

This work describes the method of synthesis and identification of the reaction products of sulfur dioxide with aqueous solutions of diethylenetriamine and bis(hexamethylene)triamine in the presence of air oxygen, new triammonium salts of diethylenetriammonium bis(sulfito)dithionate (Ia), bis trihydrate diethylenetriammonium (sulfito)-sulfate (Ib) and bis(hexamethylene)triammonium sulfate (II), respectively.

Experimental

A mixture of diethylenetriammonium bis(sulfito)-dithionate (Ia) and diethylenetriammonium bis(sulfito)-sulfate trihydrate (Ib)

A solution of DETA (0.05 mol) in 15 ml of water was poured into a thermostatically controlled cell (20^{0}C) and SO$_2$ was passed through it in the bubbling mode at a rate of 50 ml·min^{-1} for 45 min (20^{0}C). The resulting solution was kept at room temperature in air until the water was completely removed. 13.24 g of a mixture of white crystalline products Ia and Ib was isolated.

Calculated, %: C 18.72; H 6.59; N 15.57; S 22.84. Found, %: C 18.11; H 6.30; N 15.84; S 23.03.

MS (EI) I: [DETAH]$^+$ (m/z 104, I, 10%);

91, I, 16%; 89, I, 12%; [DETA−NH$_3$−H]$^+$ (85, I, 14%); [DETA−NH$_3$−2H]$^+$ (84, I, 16%); [NH$_2$CH$_2$CH$_2$NHCH$_2$]$^+$ (m/z 73, I, 44%); [SO$_2$]$^+$ (m/z 64, I, 98%); m/z 56, I, 92%; m/z 56, I, 33%; [SO]$^+$ (m/z 48, I, 46%); [CH$_3$CH=NH$_2$]$^+$ (m/z 44, I, 100%); m/z 43, I, 16%; [C$_2$H$_4$N]$^+$ (m/z 42, I, 31%); [CH$_2$=NH$_2$]$^+$ (m/z 30, I, 83%).

IR I [ν, cm^{-1}]: 3515 m., 3444 m [ν$_{as}$($\overset{+}{N}H$)]; 3034 s, 3022 s br, 3012 sh [ν$_s$($\overset{+}{N}H$)]; 2992 s br, 2984 s br [ν$_{as}$(CH$_2$)]; 2938 s br, 2905 s br, 2867 sh [ν$_s$(CH$_2$)]; 2735 s br [ν$_s$($\overset{+}{N}H$), ν$_{as}$(CH$_2$)]; 2590 m., 2209 m, 2168 sh, 2135 sh, 2123 m br, 2110 sh, 2076 sh [overtone/combination]; 1633 s [δ$_{as}$($\overset{+}{N}H_3$)]; 1603s [δ$_s$($\overset{+}{N}H_3$)]; 1580 sh [δ$_{as}$($\overset{+}{N}H_3$), δ$_{as}$($\overset{+}{N}H_2$)]; 1556 sh [δ$_s$($\overset{+}{N}H_3$), δ$_s$($\overset{+}{N}H_2$)]; 1525 s [δ$_{as}$(CH$_2$)]; 1481 s [δ$_s$(CH$_2$)]; 1456 s [ν($_C\overset{+}{N}$), δ($_C\overset{+}{N}H$)]; 1336 w. [ω(CH$_2$), ω($\overset{+}{N}H_3$), ω($\overset{+}{N}H_2$)]; 1255 s, 1225 s, 1212 s [ν$_{as}$(S$_2$O$_6^{2-}$)]; 1127 s br [ν$_{as}$(SO$_4^{2-}$), ν$_{as}$($_C\overset{+}{N}C$)]; 1078 s [ν$_s$(SO$_4^{2-}$), ν($_C\overset{+}{N}$)]; 1040 s; 1026 sh, 1006 s [ν$_{as,s}$(SO$_3^{2-}$)]; 980 s [ν$_s$(SO$_4^{2-}$), ν$_s$(SO$_3^{2-}$)]; 955 s [ν$_{as}$(SO$_3^{2-}$), ν$_s$(SO$_3^{2-}$), ν$_s$(CC), δ($\overset{+}{N}H_3$)]; 931 s br [ν$_{as}$(SO$_3^{2-}$), ν$_s$(SO$_3^{2-}$), δ($_C\overset{+}{N}$)]; 907 s [ν$_{as}$(SO$_3^{2-}$), ν$_s$(SO$_3^{2-}$)]; 894 sh; 870 s [ν$_s$(C−C−N)]; 858 sh; 848 s br [δ(C−C)]; 807 s [ν$_s$(C−N−C)]; 633 s [δ$_{as}$(SO$_4^{2-}$)]; 617 s [δ$_{as}$(SO$_4^{2-}$), δ$_s$(SO$_3^{2-}$); 566 m [δ(S$_2$O$_6^{2-}$)]; 545 w, 520 sh; 513 s [δ$_s$(SO$_4^{2-}$)]; 493 s [δ$_d$(SO$_3^{2-}$)]; 471 w [δ$_s$(SO$_4^{2-}$), δ($\overset{+}{N}-C-C-\overset{+}{N}$)]; 458 w [δ($_{C-\overset{+}{N}-C}$)].

Bis(hexamethylene) triammonium sulfate dihydrate (II)

A solution of BHMT (0.01 mol) in 30 ml of water was poured into a thermostatically controlled cell (20^{0}C) and, in the bubbling mode, SO$_2$ was passed through it at a rate of 50 ml·min^{-1} for 45 min (20^{0}C). The resulting solution was kept at room temperature in the air until the water was completely removed. The isolated white crystalline product II (4.03 g, yield 97.19%) was used without additional purification. The individuality of the obtained product was confirmed by various physical and chemical methods.

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Calculated, %: C 37.76; H 9.13; N 10,93; S 12.76. $C_{24}H_{68}N_6O_{14}S_3$. Found, %: C 37.88; H 9.01; N 11.04; S 12.64. M 761.04.

MS (EI) II: $[BHMT-H]^+$ (m/z 214, I, 10%); $[BHMD-NH_3]^+$ (m/z 198, I, 12%); m/z 129, I, 36%; m/z 112, I, 41%; $[CH_3(CH_2)_4CH=NH_2+H]^+$ (m/z 100, I, 12%); $[CH_3(CH_2)_4CH=NH_2]^+$ (m/z 99, I, 10%); $[CH_3(CH_2)_4CH=NH_2-H]^+$ (m/z 98, I, 73%); m/z 70, I, 10%; $[CH_2=CHNH=CH_2]^+$ (m/z=56, I=19%); m/z 55, I, 18%; $[CH_3CH=NH_2]^+$ (m/z 44, I, 21%); m/z 43, I, 10%; $[C_2H_4N]^+$ (m/z 42, I, 10%); m/z 41, I, 15%; $[CH_2=NH_2]^+$ (m/z 30, I, 100%).

MS (FAB) II: $[BHMT+H]^+$ (m/z 216, I, 11%).

IR II [n, cm^{-1}]: 3436 s [n(OH)]; 3246 m, 3218 sh, 3000 s, 2963 s, 2944 s, 2928 sh, 2866 m, 2809 m, 2797 m [$\nu_{as,s}(\overset{+}{N}H_2)$, $\nu_{as,s}(\overset{+}{N}H_2)$]; 2734 w [$\nu_s(\overset{+}{N}H)$, $\nu_{as}(CH_2)$]; 2621 w, 2542 w, 2473 w, 2413 w, 2021 w [overtone/combination]; 1631 m, 1594 w, 1567 sh [$\delta_{as,s}(\overset{+}{N}H_3)$, $\delta_{as,s}(\overset{+}{N}H_2)$]; 1483 m [$\delta_s(CH_2)$]; 1473 w, 1462 w, 1437 w, 1410 w, 1385 w, 1317 w [$\nu(_{C}\overset{+}{N})$, $\delta(_{C}\overset{+}{N}H)$]; 1243 sh, 1221 w [$\nu_{as}(_{C-}\overset{+}{N})$]; 1123 s [$\nu_{as}(SO_4^{2-})$]; 1072 sh [$\nu_s(SO_4^{2-})$]; 1061 w, 1049 w, 1030 w [$\nu_s(_{C-}\overset{+}{N})$]; 997 w, 973 w, 951 w, 945 w, 908 w. [$\rho(\overset{+}{N}H_3)$, $\rho(\overset{+}{N}H_2)$, $\nu_s(SO_4^{2-})$, $\rho(CH_2)$]; 619 s, 583 w [$\delta_{as}(SO_4^{2-})$]; 478 w [$\delta(\overset{+}{N}CC)$, $\delta_s(SO_4^{2-})$].

Analysis for carbon, hydrogen and nitrogen content was carried out on a CHN analyzer; sulfur was determined by the Shoniger technique [9]. IR absorption spectra were recorded on a Perkin-Elmer Spectrum BX II FT-IR System spectrophotometer in 4000−350 cm^{-1} region as KBr pellets. EI mass spectra were recorded on the MX-1321 device (direct introduction of the sample into the source, energy of ionizing electrons 70 eV). X-ray structural study of the compounds was performed on an Oxford Diffraction Ltd.Xcalibur-3 diffractometer (MoK$_\alpha$ radiation, graphite monochromator, Sapphire-3 CCD detector). X-ray powder diffraction (XRD) was accomplished on a Siemens D500 powder diffractometer (Bragg-Brentano geometry, CuK$_\alpha$ radiation, Ni filter).

Results and discussion

Mass spectra of the mixture of salts Ia and Ib and of compound II show defragmentation typical for 1-n-alkylamines [10] with the formation of the ion $[CH_2=NH_2]^+$, the peak of which has the maximum intensity for compound II. The characteristics of the fragmentation products of DETA in the mass spectrum of the mixture of its ammonium salts Ia and Ib and the tabulated mass spectrum of DETA [10] are in good agreement.

The main crystallographic data and refinement results are given in Table 1. Bond lengths and valence angles in the structures are given in Tables 2 and 3. It can be seen that these characteristics have the usual values for similar compounds (for example ref. [4]). In structure Ia, the dithionate ion is in a private position in the center of symmetry (Fig. 1). In structure Ib, the S(2)−O(4) bond of the sulfate ion is on the second-order axis (Fig. 2), so the remaining oxygen atoms of this ion are disordered. In addition, in this structure, the water molecule O(9) is also on the second-order axis. The configuration of the cation in structures Ia and Ib is markedly different. Thus, in Ib, the non-hydrogen atoms of the cation backbone lie almost in one plane (standard deviation is 0.094 Å), and in Ia the terminal nitrogen atoms deviate from the mean plane (standard deviation is 0.056 Å) of the other core atoms (N(2) and N(3) at 1.248 Å and 1.239 Å, respectively). These conformational differences can also be illustrated by data on torsion angles (Table 4): they differ little from $+180^0$ or -180^0 for the almost flat structure Ib, while these differences are significant in Ia. Layered packing is observed in both studied structures (Figs. 3 and 4). In the Ia structure, anions are arranged in layers in (001) planes, cations are located between layers of anions and form layers as well. A similar packing is observed in salt Ib: anions together with water crystallization molecules form layers parallel to (010), and layers of cations are located between them. With such a packing, a three-dimensional system of hydrogen bonds is observed in both structures, data on which are given in Tables 5 and 6. Some of these bonds are «bifurcated», or three-centered: N(2)−H(2E)···O(5) and N(2)−H(2E)···O(5)$^{-x+1,-y,-z+1}$ in Ia, N(1)−H(1A)···O(2)$^{x,-y,z+1/2}$, N(1)−H(1A)···O(1)$^{x,-y,z+1/2}$, N(2)−H(2A)···O(2)$^{-x+1/2,y+1/2,z}$, N(2)−H(2A)···O(3)$^{-x+1/2,y+1/2,z}$, N(2)−H(2C)···O(5)$^{-x+1/2,-y+1/2,z-1/2}$, N(2)−H(2C)···O(6)$^{x-1/2,-y+1/2,-z+1}$, N(3)−H(3A)···O(6) and N(3)−H(3A)···O(7)$^{-x+1,y,-z+3/2}$ in Ib. It should be noted that they are not formed in equal amounts in a mixture of compounds Ia and Ib. According to the calculation of the powder X-ray pattern by the Rietveld method using as initial data the structural models obtained by single-crystal method (Fig. 5), the reaction product contains 81.4 wt.% salt (Ia) and 18.6% salt (Ib). No other phases were found in the powder sample.

Table 1

Crystallographic data, X-ray diffraction conditions, and structure refinement characteristics for Ia and Ib

Characteristic	Values and types	
	Ia	Ib
molecular formula	$C_8H_{32}N_6O_{12}S_4$	$C_8H_{38}N_6O_{13}S_3$
M_r	532.64	522.62
T, K	293(2)	293(2)
syngony	monoclinic	rhombic
space class	C2/c	Pbcn
a, Å	28.1583(5)	18.9777(13)
b, Å	6.84450(10)	10.3131(8)
c, Å	10.8351(2)	11.5414(10)
β, deg	93.776(2)	–
V, Å^3	2083.71(6)	2258.9(3)
Z	4	4
ρ, g/cm^3	1.698	1.537
μ(MoK$_α$), mm^{-1}	0.527	0.399
θ range, deg	3.69–31.78	3.41–32.32
crystal dimensions, mm	0.35×0.20×0.15	0.40×0.25×0.15
F$_{000}$	1128	1120
T$_{min}$/T$_{max}$	0.837/0.925	0.8568/0.9426
number of reflections: measured	11832	22184
independent with з I$_{hkl}$>2σ(I)	3149	3645
R$_{int}$	0.0560	0.0488
fullness, %	95.1	96.9
number of refined parameters	141	169
R$_F$/wR^2 on observed reflections	0.0451/0.1241	0.0391/0.1077
R$_F$/wR^2 on independent reflections	0.0495/0.1304	0.0490/0.1156
S	0.992	0.982
Δρ$_{min}$/Δρ$_{max}$, e/Å^3	−0.666/0.424	−0.386/0.472

Table 2

Bond lengths and bond angles in the structure Ia*

Bond	d, Å	Bond	d, Å	Bond	d, Å
S(1)–O(2)	1.5194(12)	S(2)–O(5)	1.4799(13)	N(2)–C(2)	1.491(2)
S(1)–O(1)	1.5223(12)	S(2)–S(2)#1	2.1853(9)	N(3)–C(4)	1.481(2)
S(1)–O(3)	1.5306(12)	N(1)–C(1)	1.4887(16)	C(1)–C(2)	1.511(2)
S(2)–O(6)	1.367(2)	N(1)–C(3)	1.4951(17)	C(3)–C(4)	1.5092(19)
S(2)–O(4)	1.4709(14)				

Angle	ω, deg	angle	ω, deg
O(2)–S(1)–O(1)	105.47(7)	O(4)–S(2)–S(2)#1	102.73(6)
O(2)–S(1)–O(3)	103.94(7)	O(5)–S(2)–S(2)#1	101.76(7)
O(1)–S(1)–O(3)	104.47(7)	C(1)–N(1)–C(3)	111.60(10)
O(6)–S(2)–O(4)	126.35(14)	N(1)–C(1)–C(2)	111.98(11)
O(6)–S(2)–O(5)	108.37(13)	N(2)–C(2)–C(1)	112.71(12)
O(4)–S(2)–O(5)	112.51(8)	N(1)–C(3)–C(4)	111.62(11)
O(6)–S(2)–S(2)#1	101.32(11)	N(3)–C(4)–C(3)	112.91(12)

Note: * − symmetric transformation to obtain equivalent atoms #1 are as follows: −x+1, −y+1, −z+1.

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Table 3

Bond lengths and bond angles in the structure Ib*

Bond	d, Å	Bond	d, Å	Bond	d, Å
S(1)–O(1)	1.5093(9)	S(2)–O(7)#1	1.427(2)	N(1)–C(1)	1.4785(14)
S(1)–O(3)	1.5112(9)	S(2)–O(7)	1.427(2)	N(2)–C(2)	1.4716(14)
S(1)–O(2)	1.5331(9)	S(2)–O(4)	1.4555(12)	N(3)–C(4)	1.4599(16)
S(2)–O(5)	1.4256(17)	S(2)–O(6)	1.495(2)	C(1)–C(2)	1.5040(16)
S(2)–O(5)#1	1.4257(17)	S(2)–O(6)#1	1.495(2)	C(3)–C(4)	1.5053(16)
S(2)–O(7)#1	1.427(2)	N(1)–C(3)	1.4757(14)		
angle	ω, deg			angle	ω, deg
O(1)–S(1)–O(3)	105.82(5)			O(4)–S(2)–O(6)	107.03(9)
O(1)–S(1)–O(2)	104.60(5)			O(5)#1–S(2)–O(6)#1	107.70(14)
O(3)–S(1)–O(2)	104.44(5)			O(7)#1–S(2)–O(6)#1	105.42(16)
O(5)#1–S(2)–O(7)#1	114.80(14)			O(7)#1–S(2)–O(6)#1	105.42(16)
O(5)–S(2)–O(7)	114.80(14)			C(3)–N(1)–C(1)	111.55(9)
O(5)–S(2)–O(4)	111.65(9)			N(1)–C(1)–C(2)	110.62(9)
O(7)–S(2)–O(4)	109.74(11)			N(2)–C(2)–C(1)	109.39(9)
O(5)–S(2)–O(6)	107.70(14)			N(1)–C(3)–C(4)	109.70(10)
O(7)–S(2)–O(6)	105.43(16)			N(3)–C(4)–C(3)	110.10(10)

Note: * − symmetric transformation to obtain equivalent atoms #1 are as follows: −x+1, y, −z+3/2.

Table 4

Torsion angles in the cation for Ia and Ib

Bond	Torsion angle	
	Ia	Ib
C(3)–N(1)–C(1)–C(2)	−173.60(11)	−178.66(10)
N(1)–C(1)–C(2)–N(2)	−68.78(15)	−178.34(9)
C(1)–N(1)–C(3)–C(4)	173.81(11)	−172.60(11)
N(1)–C(3)–C(4)–N(3)	71.13(14)	169.72(10)

Fig. 2. Atom numbering scheme and thermal ellipsoids (probability level 50%) for the structure $[(NH_3CH_2CH_2)_2NH_2]_2(SO_3)_2SO_4 \cdot 3H_2O$
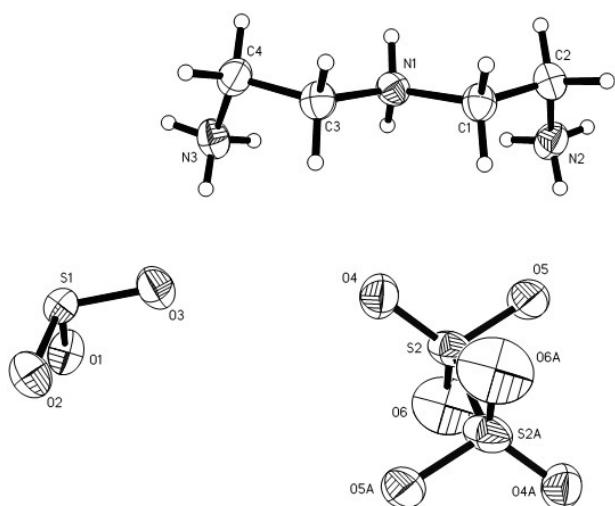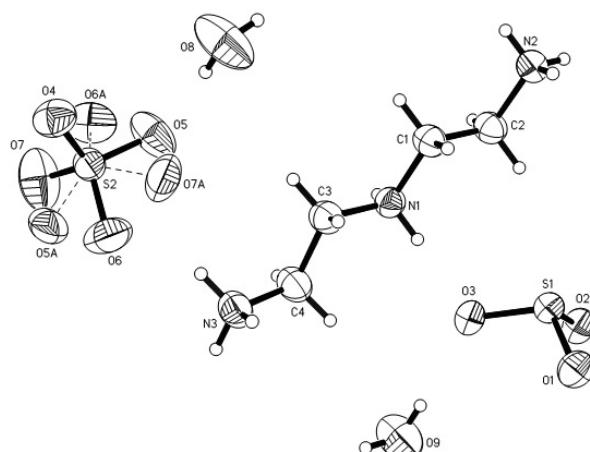
Fig. 1. Atom numbering scheme and thermal ellipsoids (probability level 50%) for the structure $[(NH_3CH_2CH_2)_2NH_2]_2(SO_3)_2S_2O_6$
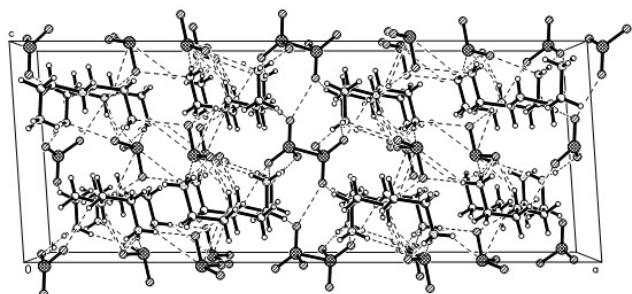
Fig. 3. Projection xy0 of the structure $[(NH_3CH_2CH_2)_2NH_2]_2(SO_3)_2S_2O_6$. Hydrogen bonds are represented by dashed lines

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Table 5

Geometrical characteristics of hydrogen bonds in the structure Ia

Contact D–H···A	Distance, Å			DHA angle, deg	Transformation for atom A
	d(D–H)	d(H···A)	d(D···A)		
N(1)–H(1A)···O(2)#2	0.90	1.94	2.8001(15)	160.3	x, y−1, z
N(1)–H(1B)···O(1)#3	0.90	1.85	2.7448(16)	177.1	x, −y+1, z+1/2
N(2)–H(2C)···O(4)#2	0.83	2.17	2.9672(18)	160.0	x, y−1, z
N(2)–H(2D)···O(3)#2	0.83	1.99	2.7291(18)	147.1	x, y−1, z
N(2)–H(2E)···O(5)	0.83	2.03	2.7964(18)	154.3	
N(2)–H(2E)···O(5)#4	0.83	2.60	3.0951(19)	119.3	−x+1, −y, −z+1
N(3)–H(3C)···O(1)#5	0.88	1.95	2.7863(17)	157.3	−x+3/2, −y+3/2, −z+1
N(3)–H(3D)···O(3)	0.88	1.88	2.7325(17)	163.2	
N(3)–H(3E)···O(2)#2	0.88	1.93	2.7740(17)	160.3	x, y−1, z

Table 6

Geometrical characteristics of hydrogen bonds in the structure Ib

Contact D–H···A	Distance, Å			DHA angle, deg	Transformation for atom A
	d(D–H)	d(H···A)	d(D···A)		
O(8)–H(8A)···O(5)	0.840(8)	2.014(8)	2.850(3)	173.5(13)	
O(8)–H(8A)···O(7)#1	0.840(8)	2.171(9)	2.918(3)	148.2(12)	−x+1, y, −z+3/2
O(8)–H(8B)···O(2)#2	0.839(7)	2.046(7)	2.8374(16)	157.2(15)	−x+1/2, −y+1/2, z+1/2
O(9)–H(9)···O(3)	0.841(8)	2.035(8)	2.8701(13)	171.5(16)	
N(1)–H(1A)···O(2)#3	0.89	1.87	2.7384(12)	167.1	x, −y, z+1/2
N(1)–H(1A)···O(1)#3	0.89	2.58	3.1813(13)	125.3	x, −y, z+1/2
N(1)–H(1B)···O(3)	0.89	1.82	2.6948(12)	170.3	
N(2)–H(2A)···O(2)#4	0.85	1.99	2.8405(13)	174.3	−x+1/2, y+1/2, z
N(2)–H(2A)···O(3)#4	0.85	2.59	3.1108(13)	120.2	−x+1/2, y+1/2, z
N(2)–H(2B)···O(1)#2	0.85	1.94	2.7675(13)	164.9	−x+1/2, −y+1/2, z+1/2
N(2)–H(2C)···O(5)#5	0.85	1.85	2.642(2)	153.9	−x+1/2, −y+1/2, z−1/2
N(2)–H(2C)···O(6)#6	0.85	2.16	2.913(3)	146.7	X−1/2, −y+1/2, −z+1
N(3)–H(3A)···O(6)	0.92	1.85	2.717(3)	156.1	
N(3)–H(3A)···O(7)#1	0.92	1.96	2.822(3)	154.5	−x+1, y, −z+3/2
N(3)–H(3B)···O(4)#7	0.92	1.98	2.8399(13)	154.6	−x+1, −y+1, −z+1
N(3)–H(3C)···O(1)#8	0.92	1.91	2.8184(14)	170.7	−x+1, y, −z+1/2

Indication of the diffractogram lines for compound II according to the Rietveld method in the line assignment mode showed that this substance belongs to triclinic class (space group P-1, a=11.347(3) Å, b=11.00(5) Å, c=18.913(4) Å, α=95.22(3)°, β=92.52(2)°, γ=118.27(4)°, V=2191.36 Å³, Z=2).

The assignment of bands in IR spectra I and II for cations $[DETAH_3]^{3+}$ and $[BHMTH_3]^{3+}$ was made taking into account the literature data [3,11,12]. The bands observed in the IR spectrum of I in the region of 3515−2867 cm⁻¹ refer to symmetric and asymmetric valence vibrations $\nu(\overset{+}{N}H_3)$, $\nu(\overset{+}{N}H_2)$ and $\nu(CH_2)$. The bands located between 1633 and 1456 cm⁻¹ correspond to the scissoring vibrations of the , $\overset{+}{N}H_3$, $\overset{+}{N}H_2$ and CH_2 groups, and to the valence $\nu(C-N)$ and deformation $\delta(CNH)$ vibrations.

A broad intense band in the IR spectrum of dihydrate II with seven well-defined maxima in the region of 3440−2730 cm⁻¹ is associated with vibrations of $\nu(OH)$ and $\nu(NH)$ molecules of water and triammonium cation $[BHMTH_3]^{3+}$. In the interval of 1750−1500 cm⁻¹, a doublet is observed at 1631 and 1694 cm⁻¹ with a shoulder at 1567 cm⁻¹, which probably refers to overlapping scissor vibrations of NH groups and water molecules characteristic for this region, similarly [HEEDA]. A multiplet of medium and weak intensity in the region of 1483−1317 cm⁻¹

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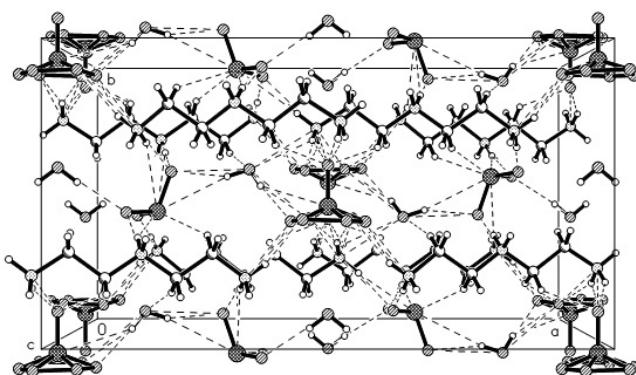
Fig. 4. Projection xy0 of the structure
$[(NH_3CH_2CH_2)_2NH_2]_2(SO_3)_2SO_4\cdot3H_2O$. Hydrogen bonds are
shown by dashed lines
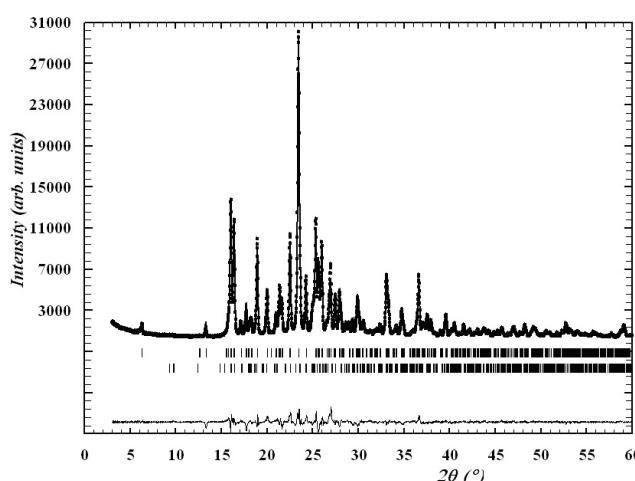
Fig. 5. Rietveld refinement for powder diffractogram of sample
I. Dots show experimental curve, solid line displays
calculation. Arrays of vertical bars show diffraction maxima
(upper row for Ia, and lower row for Ib). The lower curve
displays the difference between experimental and calculated
intensity values in each point

can be attributed to mixed valence-deformation vibrations $\nu(_C\overset{+}{N})$ and $\delta(CH)$.

In the IR spectrum of the mixture of salts Ia and Ib, the valence vibrations $\nu(SO)$ of the SO_3^{2-} (ν_1 and ν_3, respectively) are represented by intense bands at 955 cm^{-1}, 931 cm^{-1} and 907 cm^{-1}; there are also bands of lower intensity at 1026 and 1006 cm^{-1} in this region. Two bands of medium and strong intensity

at 566 and 493 cm^{-1} can be considered as the result of the splitting of the doubly degenerate out-of-plane deformation vibration ν_4 (E) of $S_2O_6^{2-}$ ion. There are strong bands at 1127 and 1078 cm^{-1} in the IR spectrum of I, corresponding to vibrations ν_{as} and $\nu_s(SO_4^{2-})$, respectively. The increased intensity of these bands (the strongest in the spectrum) is obviously due to the fact that vibrations $\nu(_C\overset{+}{N})$ also contribute to them. The decrease in symmetry of anion as a result of salt formation is accompanied by the appearance of a strong band of fully symmetric valence vibration ν_1 (A$_1$) at 980 cm^{-1}. The salt with BHMT has also the most intense band at 1123 cm^{-1} ($\nu_{as}(SO_4^{2-})$); and $\nu_1(A_1)$ is observed as a band of medium intensity at 980 cm^{-1}.

The IR spectrum of the mixture of Ia and Ib, similarly to results presented in ref. [4], has the bands in the region around 1210−1255 cm^{-1} and 570 cm^{-1}, which can be attributed to $\nu_{as}(S_2O_6^{2-})$ and $\delta(S_2O_6^{2-})$, respectively, which confirms the presence in the obtained products along with bis-sulfite (Ia) and (bis)sulfite-sulfate (Ib) anions of dithionate anions.

Thus, taking into account the data of [13], chemisorption of SO$_2$ by an aqueous solution of DETA produces ammonium hydrosulfite $[H_3NCH_2CH_2NHCH_2CH_2NH_3](HSO_3)_2$, in which terminal nitrogen atoms are obviously protonated, similar to sulfite $H_3NCH_2CH_2NHCH_2CH_2NH_3](SO_3)\cdot H_2O$ [6]. In the process of keeping the SO$_2$−DETA−H$_2$O reaction mixture in air, two mixed salts are formed as follows:

$$4[H_3NCH_2CH_2NHCH_2CH_2NH_3](HSO_3)_2+O_2\rightarrow$$
$$\rightarrow2[H_3NCH_2CH_2NH_2CH_2CH_2NH_3]_2(SO_3)_2S_2O_6+$$
$$+H_2O, \qquad\qquad\qquad (1)$$

$$4[H_3NCH_2CH_2NHCH_2CH_2NH_3](HSO_3)_2+O_2+H_2O\rightarrow$$
$$\rightarrow2[H_3NCH_2CH_2NH_2CH_2CH_2NH_3]_2(SO_3)_2SO_4\cdot3H_2O+$$
$$+SO_2\uparrow, \qquad\qquad\qquad (2)$$
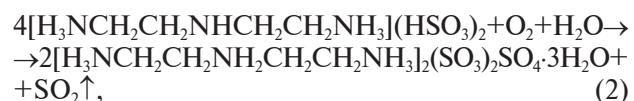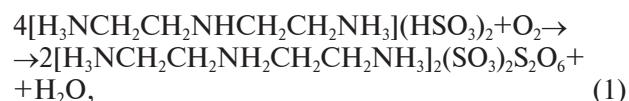
and the degree of conversion by reaction (1) is 4.3 times greater than by reaction (2). In the case of lipophilic BHMT (logP$_{ow}$=1.30[1]), sulfoxidation process S(IV)→S(VI) runs more completely, like hexamethylenediamine [9] (logP$_{ow}$=0.40[2]), as opposed to hydrophilic DETA (logP$_{ow}$=−1.30).

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[1] Reaction mass of 7-azatridecane-1,13-diamine and hexamethylenediamine. Available from: https://echa.europa.eu/bg/registration-dossier/-/registered-dossier/14602/4/8/.

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АМОНІЄВІ СОЛІ СІРКОВМІСНИХ ОКСИАНІОНІВ − ПРОДУКТИ ВЗАЄМОДІЇ ДІОКСИДУ СІРКИ З ВОДНИМИ РОЗЧИНАМИ ДІЕТИЛЕНТРИАМІНУ ТА БІС(ГЕКСАМЕТИЛЕН)ТРИ АМІНУ

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При взаємодії в системі «діоксид сірки–діетилентри-амін (або біс-(гексаметилен)триамін)–вода–кисень повітря» утворюються суміш подвійних солей (біс(сульфіто)-ди-тіонату діетилентриамонію (Ia) та тригідрату біс(сульфіто)-сульфату діетилентриамонію (Ib)) або сульфат біс(гекса-метилен)триамонію (II). Одержані амонієві солі сірковмісних оксианіонів Ia, Ib та II охарактеризовано методами еле-ментного аналізу, РСА, РФА, ІЧ-спектроскопії та мас-спектрометрії. Сполука Ia кристалізується у моноклинній сингонії (просторова група C2/c, a=28.1583(5) Å, b=6.84450(10) Å, c=10.8351(2) Å, β=93.776(2)⁰, V=2083.71(6) Å³, Z=4), Ib − у ромбічній (просторова група Pbcn, a=18.9777(13) Å, b=10.3131(8) Å, c=11.5414(10) Å, V=2258.9(3) Å³, Z=4), а II − триклинній (просторова група P-1, a=11,347(3) Å, b=11,700(5) Å, c=18,913(4) Å, α=95.22(3)⁰, β=92,52(2)⁰, γ=118,27(4)⁰, V=2191,36 Å³, Z=2). В ІЧ-спектрі суміші солей Ia та Ib валентні коливання ν (SO) сульфіт аніона (ν₁ та ν₃) надані смугами при 955, 931, 907, 1026 та 1006 см⁻¹. Дві смуги при 566 та 493 см⁻¹ – це результат розщеплення двічі виродженого позаплощинного деформаційного коливання ν₄ (E) диті-онат аніона. Смуги при 1127 та 1078 см⁻¹ відповідають коливанням νₐₛ та νₛ (SO₄²⁻). Зниження симетрії аніона SO₄²⁻ в результаті солеутворення супроводжується появою в його спектрі смуги ν₁ (A₁) при 980 см⁻¹.

Ключові слова: діоксид сірки; 2-гідроксипропіламін; біс(гексаметилен)триамін; сульфоокиснення; спектральні характеристики.

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AMMONIUM SALTS OF SULFUR-CONTAINING OXYANIONS RESULTING FROM REACTION OF SULFUR DIOXIDE WITH AQUEOUS SOLUTIONS OF DIETHYLENTRIAMINE AND BIS(HEXAMETHYLENE)TRIAMINE

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Interaction in the system «sulfur dioxide−diethylenetriamine (or bis-(hexamethylene)triamine)−water−air oxygen» results in a mixture of double salts (diethylenetriammonium bis(sulfito)-dithionate (Ia) and bis(sulfito)-sulfate trihydrate diethylenetriammonium (Ib)) or bis(hexamethylene)triammonium sulfate (II). The obtained ammonium salts of sulfur-containing oxyanions Ia, Ib, and II were characterized by the methods of elemental analysis, X-ray structural analysis, X-ray powder diffraction, IR spectroscopy, and mass spectrometry. Compound Ia crystallizes in monoclinic syngony (space group C2/c, a=28.1583(5) Å, b=6.84450(10) Å, c=10.8351(2) Å, β=93.776(2)⁰, V=2083.71(6) Å³, Z=4). Compound Ib crystallizes in rhombic syngony (space group Pbcn, a=18.9777(13) Å, b=10.3131(8) Å, c=11.5414(10) Å, V=2258.9(3) Å³, Z=4). Compound II crystallizes in triclinic syngony (space group P-1, a=11.347(3) Å, b=11.700(5) Å, c=18.913(4) Å, α=95.22(3)⁰, β=92,52(2)⁰, γ=118,27(4)⁰, V=2191,36 Å³, Z=2). The IR spectrum of the mixture of salts Ia and Ib shows the valence vibrations of ν (SO) of sulfite anion (ν_1 and ν_3), represented by bands at 955, 931, 907, 1026, and 1006 cm⁻¹. Two bands at 566 and 493 cm⁻¹ are the result of the splitting of a doubly degenerate out-of-plane deformation vibration of the ν_4 (E) of dithionate anion. The bands at 1127 and 1078 cm⁻¹ correspond to the oscillations of ν_{as} and ν_s of sulfate anion (SO_4^{2-}). A decrease in the symmetry of the SO_4^{2-} anion as a result of salt formation is accompanied by the appearance of the band ν_1 (A_1) at 980 cm⁻¹ in its spectrum.

Keywords: sulfur dioxide; 2-hydroxypropylamine; bis(hexamethylene)triamine; sulfoxidation; spectral characteristics.

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