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Crystal structure and properties of urea and thiourea adducts of tetraalkyl ammonium hydrogen sulphate

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Two inclusion complexes of tetraethylammonium hydrogen sulfate ($Et_4N.HSO_4$) with thiourea (TU) and urea (U) were prepared and characterized by X-ray diffraction (XRD) and differential thermal analysis (DTA). The crystal structures of the commercial salt $Et_4N.HSO_4$ (**1**) and both of the complexes $Et_4N.HSO_4.TU.H_2O$ (**2**) and $2Et_4N.2HSO_4.H_2SO_4.3U$ (**3**) were solved. Compounds **1** and **2** crystalize in the monoclinic $P2_1/n$ space group and compound **3** in the triclinic $P\overline{1}$ one. The cations and anions in **1** display a layered-like arrangement of alternating well-ordered tetraethylammonium cations and hydrogen-bonded hydrogen sulfate anions. In **2** and **3** the anionic layer is more complex and in addition to the hydrogen sulfate it includes thiourea and water or urea molecules, respectively. The thermal behavior of both adducts is more complicated than the one of $Et_4N.HSO_4$ and the melting temperature of the studied compounds decreases in the following order: **1** > **3** > **2**.

Key words: urea, thiourea; inclusion complex; hydrogen bonding; thermal decomposition.

INTRODUCTION

Tetraethylammonium salts are used as a source of tetraethylammonium ions (Et_4N) in pharmacological and physiological studies, but also in organic chemical synthesis and as structure-directing agents for synthesis of microporous materials [1, 2]. Besides, the urea and thiourea efficiency in formation of anionic host lattices is well defined due to the high dipole moment, planar geometry and good donor-acceptor properties of both molecules. A great number of urea and thiourea crystal complexes of different tetraethylammonium salts were synthesized aiming to study their crystal structures, phase transitions and temperature stability [3–10]. Varieties of host lattices were obtained depending on the combination of the employed anion and the number of urea/thiourea molecules. For instance, the inclusion complexes of $(Et_4N)C_4O_4$ with thiourea exhibit layered, one dimensional channel and two dimensional channel structures depending on the number of the incorporated thiourea molecules [11]. Many complex anions were employed including halides [12, 13], carbonate [14], perchlorate [15], borate [16], fumarate [17], etc. However, to date no structural information about the commercially distributed $Et_4N.HSO_4$ was reported [Cambridge Structural Database (CSD), 2011 release]. Moreover, bis(tetraethylammonium) hydrogen-sulfate dihydrogen-phosphate is the only reported compound containing both the Et_4N^+ and HSO_4^- ions. [18].

The present communication concerns the preparation of two new inclusion complexes of urea and thiourea with tetraethyl ammonium hydrogen-sulfate from aqueous or water/methanol solutions. The crystal structures of the studied compounds are discussed in relation to the differences in their thermal behavior.

MATERIALS AND METHODS

Synthesis

Tetraethylammonium hydrogen-sulfate, $Et_4N.HSO_4$ (**1**) is a commercial product and crystals suitable for single crystal X-ray diffraction measurements were obtained by slowly evaporation from water solution.

The other two compounds tetraethylammonium hydrogen sulfate thiourea hydrate, $Et_4N.HSO_4.TU.H_2O$ (**2**) and tetraethylammonium hydrogen-sulfate sulfonic acide ureate, $2Et_4N.2HSO_4.H_2SO_4.3U$

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(**3**) were obtained by slow evaporation from water solution of the components at room temperature:

$Et_4N.HSO_4.TU.H_2O$ (**2**): 0. 227 g (1.10^{-3} mol) $Et_4N.HSO_4$ and 0.078 g (1.10^{-3} mol) TU are dissolved in 20 ml of distilled water. The solution is slowly evaporated at room temperature leading to the formation of prismatic colorless crystals.

$2Et_4N.2HSO_4.H_2SO_4.3U$ (**3**): 0. 227 g (1.10^{-3} mol) $Et_4N.HSO_4$ and 0.060 g (1.10^{-3} mol) U are dissolved in 20 ml of distilled water. The solution is slowly evaporated at room temperature leading to the formation of prismatic colorless crystals.

Methods

XRD single crystal analyses: Crystals of the studied compounds were mounted on glass capillaries and diffraction data were collected at room temperature by ω-scan technique, on an Agilent Diffraction SuperNova Dual four-circle diffractometer equipped with Atlas CCD detector using mirror-monochromatized MoKα radiation from micro-focus source (λ = 0.7107 Å). The determination of cell parameters, data integration, and scaling and absorption correction were carried out using the CrysAlis Pro program package [19]. The structures were solved by direct methods (SHELXS-97) [20] and refined by full-matrix least-square procedures on F^2 (SHELXL-97) [20]. The non-hydrogen atoms were refined anisotropically and urea and thiourea hydrogen atoms were placed at idealized positions and refined using the riding model. The positions of hydrogen atoms of water molecule were calculated by DHA software [21]. A summary of the structural and refinement data is provided in Table 1. The data for publication were prepared using the program package WinGX [22]. Crystallographic data were deposited with the Cambridge Crystallographic Data Centre, CCDC No. 935080 (**1**) 93508 (**2**), 935082 (**3**). A copy of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44 1223 336 033, e-mail:deposit@ccdc.cam.ac.uk., or www.ccdc.cam.ac.uk.

Table 1. Crystal data and structure refinement results for the studied compounds

CCDC deposit number	1	2	3
Empirical formula	C8 H21 N O4 S	C9 H27 N3 O5 S2	C19 H56 N8 O15 S3
Moiety formula	C8 H20 N, O4 H S	C8 H20 N, H O4 S, C H4 N2 S, H2 O	3(O4 H S), 3(C H4 N2 O), 2(C8 H20 N)
Formula weight	227.32	321.46	732.9
Temperatute (K)	290(2)	290(2)	290(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P\ 2_1/n$	$P\ 2_1/n$	$P\ -1$
a	9.7994(5)	9.4527(6)	7.4002(4)
b	13.812(3)	10.1222(6)	15.2365(8)
c	9.5968(17)	17.9932(11)	16.6134(8)
α	90	90	73.130(5)
β	89.368(15)	100.160(6)	88.137(4)
γ	90	90	84.630(4)
Volume (Å^3), Z	1190.2(4), 4	1694.63(18), 4	1784.71(16), 2
Calculated density (Mg m^{-3})	1.269	1.260	1.364
F(000)	496	696	788
Crystal color, shape, size (mm)	Colorless, prismatic 0.3 × 0.28 × 0.26	Colorless, prismatic 0.32 × 0.30 × 0.28	Colorless, prismatic 0.32 × 0.3 × 0.28
θ Range for data collection (deg)	2.95–29.58	3.52–29.12	2.99–29.45
Limiting indices h, k, l	$-12 \le h \le 11, -18 \le k \le 13, -11 \le l \le 13$	$-11 \le h \le 9, -13 \le k \le 10, -24 \le l \le 17$	$-10 \le h \le 9, -16 \le k \le 20, -22 \le l \le 22$
Reflections collected	6931	6277	14262
Independent reflections	2839	3513	7982
R_{int}	0.0446	0.0256	0.0438
Goodness-of-fit on F^2	1.058	1.047	1.019
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0937$, $wR_2 = 0.2653$	$R_1 = 0.0681$, wR2 =0.1990	$R_1 = 0.0694$, $wR_2 = 0.1809$
R indices (all data)	$R_1 = 0.1308$, $wR_2 = 0.3061$	$R_1 = 0.1106$, $wR_2 = 0.2318$	$R_1 = 0.0958$, $wR_2 = 0.2082$
Largest diff. Peak/ hole (e Å^{-3})	0.873/ −0.574	0.652/ −0.277	0.957/ −0.498

Thermal analyses: Differential thermal analysis (DTA) and thermogravimetric measurements (TG) were carried out simultaneously in a thermal analyzer Stanton Redcroft 780 at the following conditions: heating rate of 10 °C/min, dry argon as a carrier gas, Al_2O_3 used as a referring material and sample weight of 8–10 mg.

RESULTS AND DISCUSSION

The asymmetric units of the studied compounds are shown in Figures 1, 2 and 3. Table 2 gives information about the bond distances and angles for HSO_4 group, urea and thiourea molecules in compounds **1**, **2** and **3**. The three dimensional packing of the discussed compounds and their hydrogen bonding systems are presented in Figure 4 and Table. 3.

Crystal structure of $Et_4N.HSO_4$ (**1**)

Figure 1 presents the asymmetric unit of compound **1**. It crystallizes in a monoclinic $P2_1/n$ space group and has pseudo orthorhombic lattice with a beta angle of 89.4°. The bond lengths and bond angles characterizing the Et_4N cation and hydrogen-sulfate anion agree with those reported previously [1–18] (Table 2.). There are four anions and four cations in the unit cell. The smaller hydrogen sulfate ion donates and accepts a hydrogen bond to form dimers. The dimers are arranged in layers parallel to $(10\bar{1})$ and are spaced at a distance of 6.53 Å (Fig. 4a, Tabl. 3). The larger Et_4N ions have a regular "Nordic cross" like shape with S_4 symmetry (Fig. 1). They are sandwiched between the anionic layers. Thus the 3D arrangement of $Et_4N.HSO_4$ is very similar to that in $2Et_4N.HSO_4.H_2PO_4$ [18] but the hydrogen-bonding network within the anionic layers is less extensive.

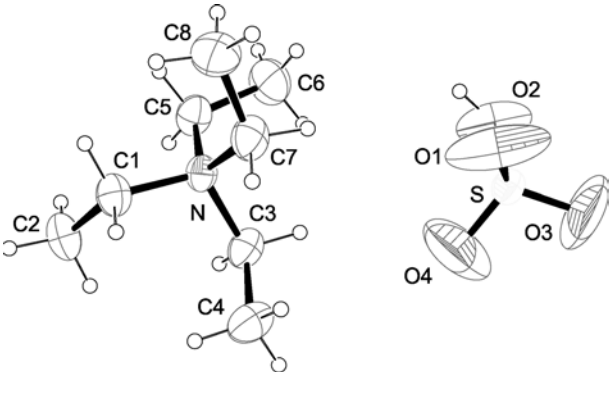

Fig. 1. ORTEP [23] view of complex ions in compound **1** with the atomic numbering scheme; ellipsoids are drawn at 50% probability; hydrogen atoms are shown as small spheres with arbitrary radii

Crystal structure of $Et_4N.HSO_4.TU.H_2O$ (**2**)

The TU adduct crystallizes as a neutral molecular adduct with one water molecule (Fig. 2). The crystal structure is monoclinic, space group $P2_1/n$ and there are four structural units per unit cell. The 3D arrangement is the same as in compound **1** and the larger Et_4N^+ ions are sandwiched between the layers built by hydrogen-sulfate anions and the rest of the molecules. As it is expected the TU and H_2O molecules are incorporated within the HSO_4^- layers

Table 2. Selected geometric parameters for the studied compounds. Bond lengths (Å)

Compound 1			
S – O(1)	1.409(5)	N – C(5)	1.505(5)
S – O(2)	1.515(4)	N – C(7)	1.512(5)
S – O(3)	1.310(5)	C(1) – C(2)	1.481(6)
S – O(4)	1.340(6)	C(3) – C(4)	1.497(7)
N – C(1)	1.515(5)	C(5) – C(6)	1.508(7)
N – C(3)	1.523(5)	C(7) – C(8)	1.504(8)
Compound 2			
S – O(1)	1.492(3)	C(11) – C(12)	1.529(8)
S – O(2)	1.435(3)	C(13) – C(14)	1.580(9)
S – O(3)	1.484(3)	C(15) – C(16)	1.574(9)
S – O(4)	1.433(3)	C(17) – C(18)	1.525(9)
N – C(11)	1.530(6)	S(1) – C(1)	1.696(4)
N – C(13)	1.474(7)	C(1) – N(11)	1.318(4)
N – C(15)	1.511(6)	C(1) – N(12)	1.326(4)
N – C(17)	1.554(7)		
Compound 3			
S(1) – O(11)	1.507(2)	C(11) – C(12)	1.514(5)
S(1) – O(12)	1.456(2)	C(13) – C(14)	1.509(7)
S(1) – O(13)	1.459(2)	C(15) – C(16)	1.505(5)
S(1) – O(14)	1.452(2)	C(17) – C(18)	1.499(6)
S(2) – O(21)	1.484(2)	C(21) – C(22)	1.516(6)
S(2) – O(22)	1.449(2)	C(23) – C(24)	1.507(6)
S(2) – O(23)	1.485(2)	C(25) – C(26)	1.499(6)
S(2) – O(24)	1.449(2)	C(27) – C(28)	1.499(6)
S(3) – O(31)	1.423(3)		
S(3) – O(32)	1.426(4)	O(1) – C(1)	1.289(4)
S(3) – O(33)	1.500(3)	O(2) – C(2)	1.302(4)
S(3) – O(34)	1.396(3)	O(3) – C(3)	1.302(4)
N(1) – C(11)	1.514(4)	C(1) – N(11)	1.325(4)
N(1) – C(13)	1.522(4)	C(1) – N(12)	1.314(4)
N(1) – C(15)	1.515(4)	C(2) – N(21)	1.295(4)
N(1) – C(17)	1.513(4)	C(2) – N(22)	1.304(4)
N(2) – C(21)	1.509(4)	C(3) – N(31)	1.305(4)
N(2) – C(23)	1.520(4)	C(3) – N(32)	1.310(4)
N(2) – C(25)	1.518(4)		
N(2) – C(27)	1.517(4)		

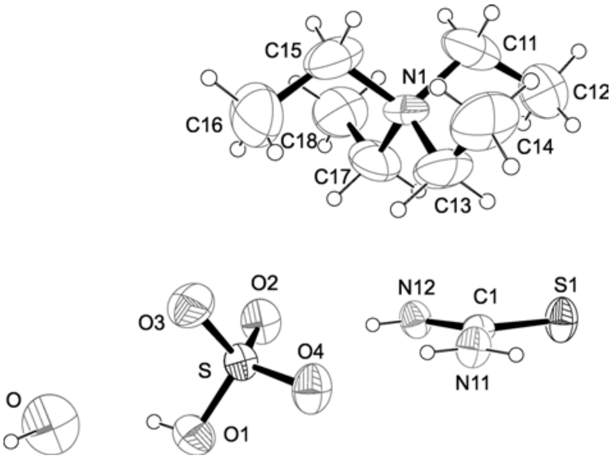

Fig. 2. ORTEP [23] view of complex ions and molecules in compound **2** with the atomic numbering scheme; ellipsoids are drawn at 50% probability; hydrogen atoms are shown as small spheres with arbitrary radii

Table 2. Selected geometric parameters for the studied compounds. Bond lengths (Å)

Compound 1			
S – O(1)	1.409(5)	N – C(5)	1.505(5)
S – O(2)	1.515(4)	N – C(7)	1.512(5)
S – O(3)	1.310(5)	C(1) – C(2)	1.481(6)
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S – O(3)	1.484(3)	C(15) – C(16)	1.574(9)
S – O(4)	1.433(3)	C(17) – C(18)	1.525(9)
N – C(11)	1.530(6)	S(1) – C(1)	1.696(4)
N – C(13)	1.474(7)	C(1) – N(11)	1.318(4)
N – C(15)	1.511(6)	C(1) – N(12)	1.326(4)
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S(2) – O(21)	1.484(2)	C(21) – C(22)	1.516(6)
S(2) – O(22)	1.449(2)	C(23) – C(24)	1.507(6)
S(2) – O(23)	1.485(2)	C(25) – C(26)	1.499(6)
S(2) – O(24)	1.449(2)	C(27) – C(28)	1.499(6)
S(3) – O(31)	1.423(3)		
S(3) – O(32)	1.426(4)	O(1) – C(1)	1.289(4)
S(3) – O(33)	1.500(3)	O(2) – C(2)	1.302(4)
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N(2) – C(25)	1.518(4)		
N(2) – C(27)	1.517(4)		

and are involved in the hydrogen bonding network, which in this case is distributed over the whole layer (Fig. 4b, Table. 2). Thus, although the layer has similar thickness as in compound **1** the stacking is realized at a longer distance (7.64 Å in **2** versus 6.53 Å in **1**). This is accompanied with less compact shape of Et_4N ion exhibiting D2d symmetry in this structure (Fig. 2). The N….N distance between the closest Et_4N cations is 7.43Å, while the corresponding distance in compound **1** is 6.64 Å.

Crystal structure of $2Et_4N.2HSO_4.H_2SO_4.3$Urea (**3**)

The asymmetric unit is presented in Figure 3. The organization of the crystal structure in this compound is very similar to that in **1** and **2**, but it crystallizes in triclinic P–1 space group. The sulfate groups and urea molecules are hydrogen bonded and built negatively charged layers, between which Et_4N^+ cations are situated. The hydrogen bonding network is presented in Fig. 4c. Hydrogen-sulfate groups and urea molecules are hydrogen-bonded to form anionic layers spaced at 8.30 Å from each other. The Et_4N cations are placed between the layers and the N…N distance between the closest ones is 7.40 Å. This is in agreement with the shape of Et_4N having D2d symmetry as in compound **2**. The structure determination shows a deficiency of Et_4N^+ ions and in order to balance the electro-neutrality of the compound it is assumed that it crystalizes with one molecule of sulfuric acid. However, this could not be confirmed by the X-ray diffraction data, because it was not possible to localize the positions of H atoms from the electron density map. On the other hand, the S-O distances for the symmetrically nonequivalent sulfate groups can give information about the presence of OH group because the corresponding S-O bond distance should be longer than the other three ones. This is actually the case for $(S2)O_4$ sulfate group only (Table 2). In contrast, the four S-O bonds in the $(S1)O_4$ and $(S3)O_4$ groups have similar lengths of about 1.46 Å. One possible explanation is that there is a migration of protons along the strong O-H…O hydrogen bonds formed between sulfate and urea oxygen atoms (Table 3). Besides, C-O distances in all of the urea molecules are longer than the standard C=O double bond (~1.2 Å) and have values of about 1.3 Å.

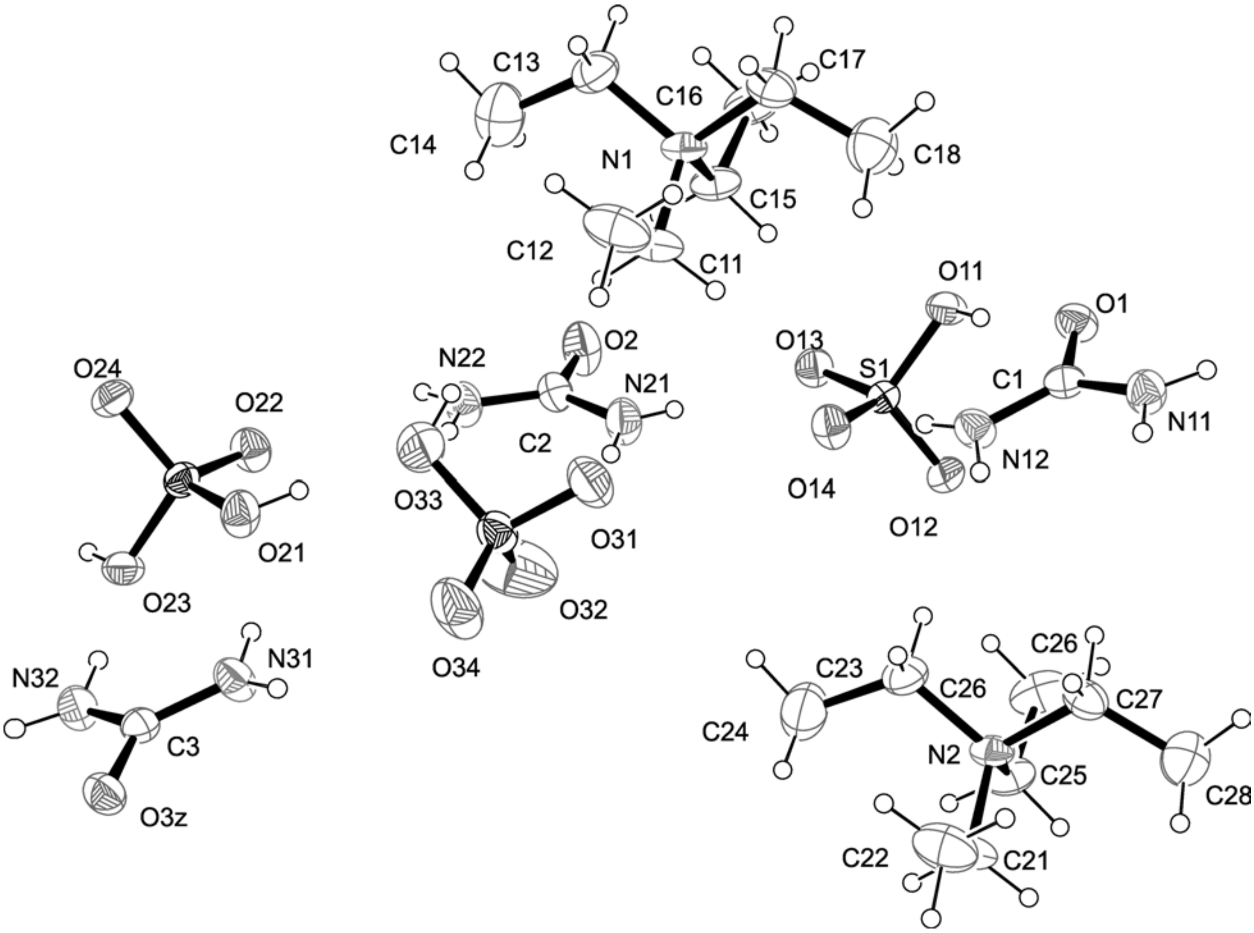

Fig. 3. ORTEP [23] view of complex ions and molecules in compound **3** with the atomic numbering scheme; ellipsoids are drawn at 50% probability; hydrogen atoms are shown as small spheres with arbitrary radii

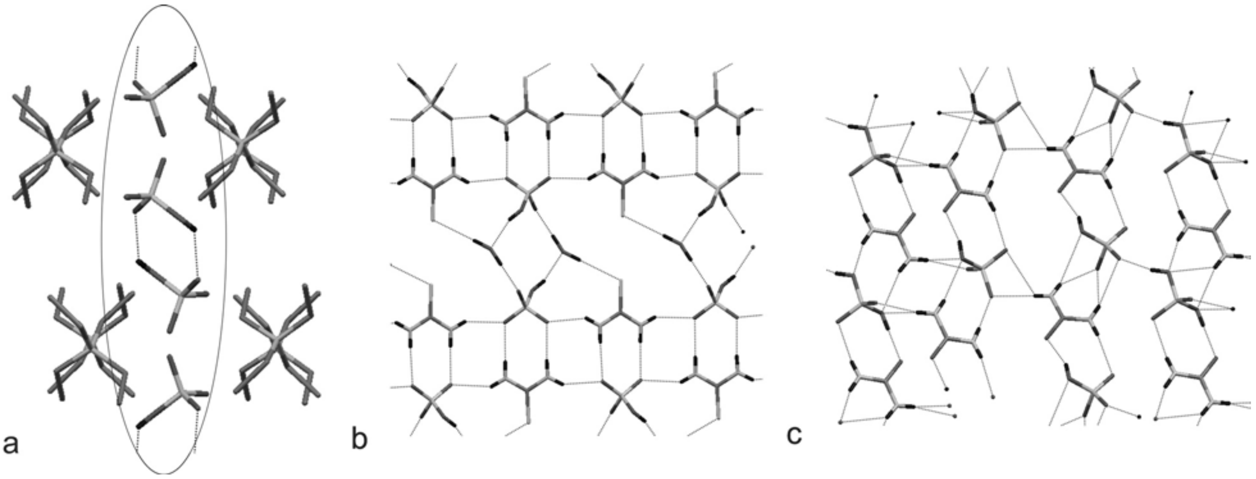

Fig. 4. Three dimensional packing and hydrogen bonding systems: a) stacking of cationic and anionic layers with hydrogen bonds between HSO_4 groups compound **1**; b) hydrogen-bonding system within the complex layer in compound **2**; c) hydrogen-bonding system within the complex layer in compound **3**

Table 3. Hydrogen-bond geometry (Å, °) for:

Compound 1

D—H…A	*D—H*	H…A	D…A	D—H…A
O2-H2…O1^{i}	0.820	1.876	2.479	129.48

i: –x+1, –y +1, –z+1

Compound 2

D—H…A	*D—H*	H…A	D…A	D—H…A
O-H1…S1^{i}	0.960	2.490	3.450	179.60
O-H2…O3^{ii}	0.961	1.725	2.686	179.81
O1-H1A…O	0.820	1.864	2.644	158.32
N11-H11C…O4	0.860	2.127	2.977	169.51
N11-H11D…O2^{iii}	0.860	2.171	2.932	147.25
N12-H12D…O2	0.860	2.113	2.966	171.77
N12-H12E…O4^{iv}	0.860	2.145	2.916	149.12

i: –x+3/2, y–1/2, –z+1/2; ii: –x, –y+1, –z+1; iii: –x+3/2, y+1/2, –z+1/2;
iv: –x+3/2, y–1/2, –z+1/2

Compound 3

D—H…A	*D—H*	H…A	D…A	D—H…A
O11-H11…O1	0.820	1.681	2.483	164.99
O21-H21…O33	0.820	1.706	2.512	167.15
O23-H23…O3^{i}	0.820	1.734	2.537	165.91
O31-H31…O2^{ii}	0.820	1.725	2.494	155.42
N11-H11C…O24^{iii}	0.852	2.079	2.920	168.75
N11-H11D…O11^{ii}	0.815	2.354	3.154	167.12
N12-H12D…O13^{ii}	0.805	2.047	2.851	176.37
N12-H12E…O14	0.813	2.036	2.830	165.22
N22-H22D…O32	0.812	2.133	2.920	163.27
N22-H22E…O34^{i}	0.794	2.505	3.143	138.46
N22-H22E…O33	0.794	2.558	3.294	154.93
N21-H21C…O13	0.745	2.130	2.875	176.81
N21-H21C…O14	0.745	2.657	3.124	122.75
N21-H21D…O32	0.743	2.238	2.926	154.45
N31-H31A…O21	0.874	2.051	2.896	162.17
N31-H31B…O22^{ii}	0.796	2.083	2.862	165.67
N32-H32A…O23	0.848	2.348	3.162	161.09
N32-H32A…O21	0.848	2.648	3.354	141.57
N32-H32B…O12^{iv}	0.816	2.049	2.856	170.33

i: x+1, y, z; ii: x–1, y, z; iii: x–1, y+1, z; iv: x, y–1, z;

Thermal behavior

The thermal behavior of compounds **1**, **2** and **3** is investigated between room temperature and 400 °C using DTA-TG-DTG analysis (Fig. 5).

Compound **1**: DTA measurement shows a slow endothermic effect at 160 °C without loss of mass on the TG curve. Such kind of effect, assigned to phase transition, has been reported to be at 189 °C for tetramethylammonium sulfate [25] and in the interval 154–170 °C for tetraethylammonium tetrachloro-, bromotrichloro- and tribromochloroferrates(III) [26]. In the last work additional endo-effects corresponding to the melting point of the compounds are observed between 265–283 °C. However, in DTA curve of compound **1** similar effect cannot be clearly defined, because the melting and the main decomposition of the compound seem to occur simultaneously. These processes manifest a sequence of exo- and endo-effects maximizing at 297 and 330 °C, respectively, and are related to about 70% mass loss, which corresponds to a partial degradation. The described thermal behavior is rather similar to that in [26], where the thermal decomposition of tetraethylammonium salts had occurred in two main steps: first one, maximazing at 380–390 °C and corresponding to 60–79% mass loss and the second one – much slower, coming to an end at 700 °C and relating to the remaining sample mass loss.

The thermal behavior of compounds **2** and **3** (Fig. 5) becomes more complicated as compared with that of **1** and shows a complete degradation up to 400 °C. The first endothermic effect in the DTA curve (due to the melting of compounds without

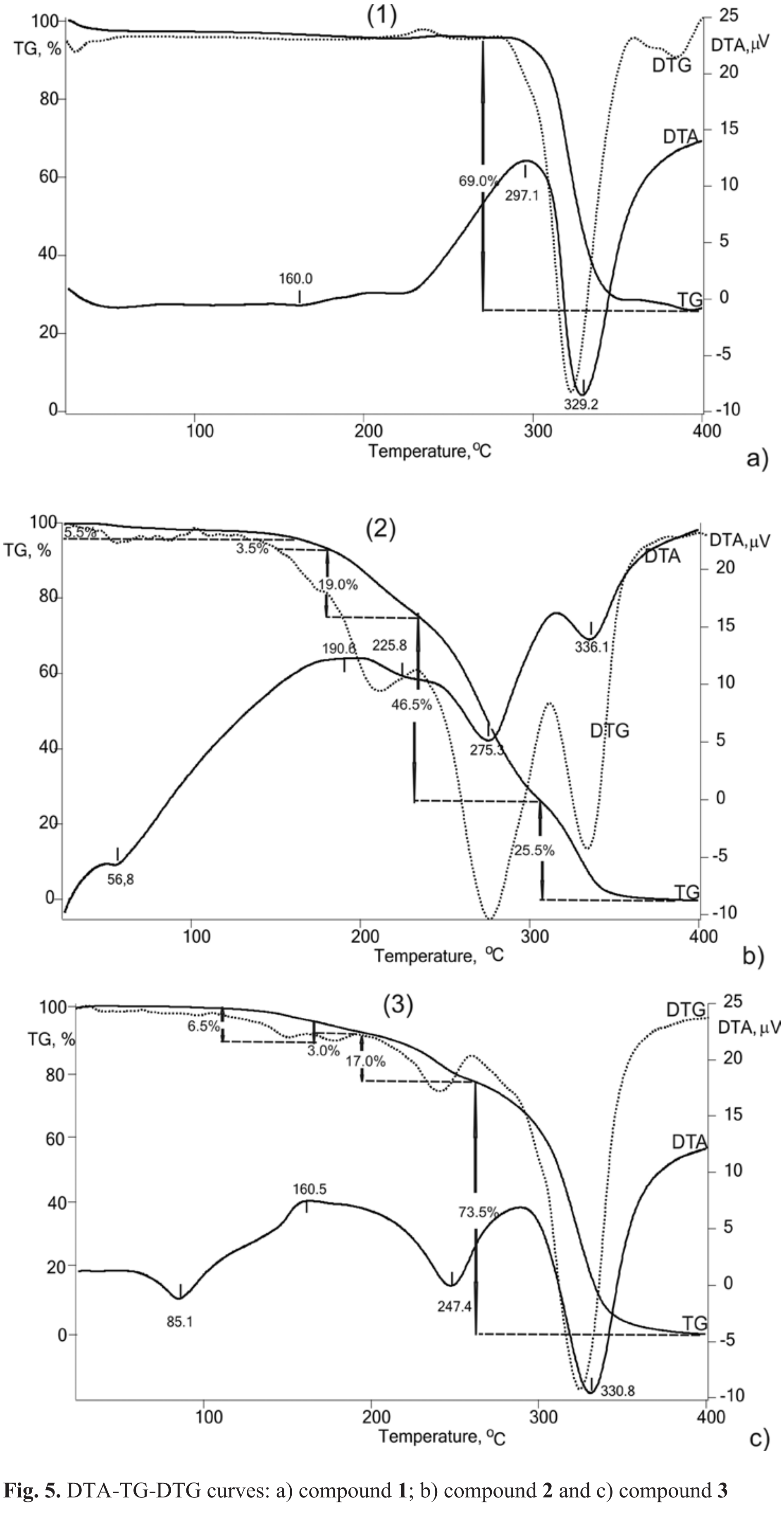

Fig. 5. DTA-TG-DTG curves: a) compound **1**; b) compound **2** and c) compound **3**

mass loss on the TG curves) of compounds **2** and **3** appears at 57 °C and 85 °C respectively, while the melting point of pure thiourea and urea has been observed respectively at 158 °C [27] and 132 °C [28]. Most probably, the presence of crystallization water in compound **2** decreases the melting temperature of that compound. At the same time the water in this sample continuously releases up to 150 °C with mass loss of about 5%, which corresponds to 1 molecule of H_2O (Fig. 5b). The melting temperature of the studied compounds decreases in the order: **1** > **3** > **2**.

As it is evident from the DTA-TG-DTG curves at least four events occur during the decomposition of both adducts being more clearly separated in compound **2** (Figures 5b and 5c). The process starts after the compound's melting with exothermal event on DTA curves following by series of endothermal events. These events manifest at lower tempereatures for the urea adduct (compound **3)** comparing with the thiourea one (compound **2)**.

The thermal degradation of tetraethylammonium salts has been investigated ever since the beginning of 20th century [29]. Two main ways of degradation have been defined both related to generation of a tertiary amine: beta degradation known also as "Hofmann degradation" and a nucleophilic substitution [30]. However, the decomposition processes of the studied compounds are more complicated due to the complex degradation of the HSO_4 group and the presence of Urea or Thiourea molecules.

CONCLUSIONS

Urea and Thiourea adducts of $Et_4N.HSO_4$ were synthesized and the crystal structures of the initial alkyl-ammonium salt and both adducts $Et_4N.HSO_4.TU.H_2O$ and $2Et_4N.2HSO_4.H_2SO_4.3U$ were solved. The structural analyses show that all three compounds have similar structures, where the large Et_4N cations are sandwiched between layers of hydrogen bonded anions or anions and molecules. The cation shape depends on the free space between the layers. In the initial alkyl-ammonium salt Et_4N has "Nordic cross" shape with 4s symmetry, while in both adducts it becomes less compact and has D2d symmetry.

The most complicated hydrogen bonding system with strong O–H…O bonds is observed in the Urea containing adduct. This supposes higher stability of that configuration compared to the thiourea compound, which is confirmed by the thermal analyses data. The structural features affect the melting point of the studied compounds and the observed melting temperature decreases in the following order: $Et_4N.HSO_4 > 2Et_4N.2HSO_4.H_2SO_4.3U > Et_4N.HSO_4.TU.H_2O$.

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КРИСТАЛНА СТРУКТУРА И СВОЙСТВА НА УРЕА И ТИОУРЕА АДУКТИ НА ТЕТРАЕТИЛ АМОНИЕВ ХИДРОГЕН-СУЛФАТ

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(Резюме)

Синтезирани са две съединения на тетраетил-амониев-хидроген сулфат ($Et_4N.HSO_4$) с тиоуреа (TU) и уреа (U). Първоначалния продукт тетраетил-амониев-хидроген сулфат ($Et_4N.HSO_4$) и двете нови съединения са характеризирани чрез рентгеноструктурен (XRD) и термичен (DTA-TG) анализи. Определени са кристалните структури на търговския продукт $Et_4N.HSO_4$ (**1**) и двете нови съединения $Et_4N.HSO_4.TU.H_2O$ (**2**) и $2Et_4N.2HSO_4.H_2SO_4.3U$ (**3**). Съединенията **1** и **2** кристализират в моноклинна пространствена $P2_1/n$, а съединения **3** в триклинна пространствена група $P\bar{1}$. Катионите и анионите в съединение **1** оформят слоисто-подобна структура в която се редуват слоеве от тетраетил-амониви катиони и свързани с водородни връзки хидроген-сулфатни аниони. Кристалните структури на новосинтезираните материали са подобни на тази на съединение **1**, но анионните слоеве има по-комлексен строеж, поради наличието на тиоуреа и вода или уреа молекули за съединения **2** и **3** съответно. Термичното поведение на двата адукта е по-сложно в сравнение с това на първоначалния продукт $Et_4N.HSO_4$, като температурата на топене на изследваните съединения намалява в посочената последователност: **1** > **3** > **2**.