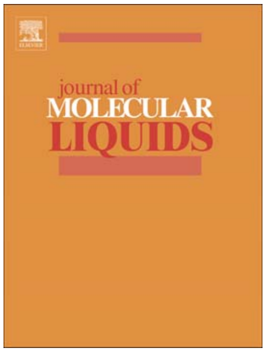

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Triethanolammonium salicylate – protic alkanolammonium ionic liquid

Y. Kondratenko[1*], T. Kochina[1,2], V. Fundamensky[1,3], I. Ignatyev[2], T. Panikorovskii[4], G. Nyanikova[3]

[1] *Grebenshchikov Institute of Silicate Chemistry RAS, nab. Makarova, 2, St. Petersburg, 199034 Russia*
[2] *Department of radiochemistry, Institute of Chemistry, St. Petersburg State University, 7/9 University emb., St. Petersburg 199034, Russia.*
[3] *St. Petersburg Stt. Inst. Technol., Moskovskii pr. 26, St. Petersburg, Russia*
[4] *Department of Crystallography, Institute of Earth Sciences, St. Petersburg State University, University Emb., 7/9, 199034 St. Petersburg, Russia*
[*] *Corresponding author. Tel.:+78123284802, e-mail: kondratencko.iulia@yandex.ru*

Keywords: triethanolammonium salicylate; protatrane; ionic liquid; synthesis; structure; antifungal activity.

Abstract

Triethanolammonium salicylate was synthesized, characterized by IR and NMR spectroscopy. The structure was established, and cation-anion interactions were investigated by X-ray diffraction analysis. It was found that exchange reaction occurs at triehanolammonium salts interaction with silver (I) nitrate, and the product structure was established by X-ray diffraction analysis. The influence of triethanolammonium salicylate solution on the growth properties of the fungus Rhizopus oryzae was studied.

1. Introduction

Ionic liquids (ILs) are a class of relatively novel compounds comprising bulky, organic cations and inorganic or organic anions. [1-3] Ionic liquids have attracted much attention in various fields of science and technology (electrochemistry, catalysis and organic synthesis, electrochemical sensors, and other areas) due to their unique properties as suitable solvents for a broad scope of inorganic, organic and polymeric materials. Their features such as high polarity, chemical and thermal stability, as well as a wide interval of liquid state, [1-6] draw interest to them of the large scope of chemist. Also, in recent years, ILs have attracted attention due to the possibility of the design of a new compounds with unique properties, e.g., pharmacologically active ionic liquids by combining cations and anions with desired properties [7-9].

Triethanolammonium salts of protic acids belong to the class of protic alkanolammonium ionic liquids [10, 11], and due to their unique atrane structure became known as protatranes [12, 13]. A number of studies have shown [14-18] that many protatranes have biological activity, which is mainly determined by the atrane structure of the cation and the nature of an anion. The first compound of this class was triethanolammonium salt of 2-methylphenyloxyacetic acid [2-$CH_3C_6H_4OCH_2COO]^-$ $[NH(CH_2CH_2OH)_3]^+$ (trecrezan), which is a drug of wide spectrum of action (adaptogen, immunomodulator, etc.) [17, 18].

As determined by X-ray diffraction analysis [12, 19-27] protatrane cation $[NH(CH_2CH_2OH)_3]^+$ has a tricyclic structure with N→H bond, directed inward the protatrane framework. Three oxygen atoms from hydroxyethyl groups (CH_2CH_2OH) of protatrane cation, which surround the hydrogen atom of NH group, form three intramolecular trifurcate hydrogen bonds (*endo*-configuration, figure 1).

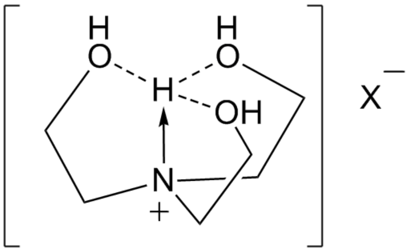

Figure 1

Most of the known triethanolammonium salts have such atrane structure (figure 1). These salts are formed by triethanolammonium cation $[NH(CH_2CH_2OH)_3]^+$ and inorganic (X =Hal [23-25], NO_3 [26], ClO_4 [22], etc.) or organic (X = 2-$CH_3C_6H_4OCH_2COO$ [19], 4-$ClC_6H_4SCH_2COO$ [20], HOOCCOO [27], $HOOCCH_2COO$ [27], $C_6H_4(HCO)COO$ [28]) anions.

In the last work [28] the structure of triethanolammonium 2-formylbenzoate was established by X-ray diffraction analysis. Triethanolammonium cation in this salt has structure that differs significantly from other protatranes, since two CH_2CH_2OH branches are directed along the NH group *(endo*-branches), but the third branch *(exo*-branch) is pointed in a reverse direction. In this molecule the existence of the *exo*-branch is conditioned by a hydrogen bond (1.79 Å) between the hydroxyl group of protatrane cation and the oxygen atom of the 2-formylbenzoate anion. Thus, the cation in this salt has an *exo-endo* conformation (figure 2).

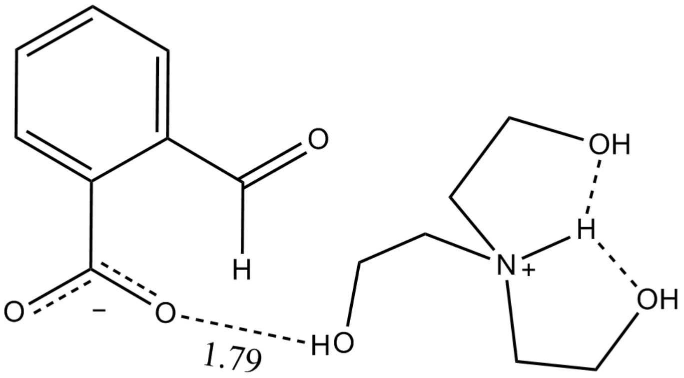

Figure 2

In this study we synthesized and characterized by IR and NMR spectroscopy a new triethanolammnium salt of salicylic acid which belongs to the class of protic alkanolammonium ILs. The structure of this compound was determined by single crystal X-ray diffraction analysis.

The anion of this salt, as in the case of triethanolammonium 2-formylbenzoate, has the substituent (OH-group) at the second carbon atom of aromatic ring. Therefore, it is interesting to investigate the effect of this anion on the structure of protatrane cation. The other aim of this study was to prepare a new silver-containing compounds based on triethanolammonium salts, and to investigate the interaction of triethanolammonium salicylate with silver (I) nitrate in polar medium (ethanol). In addition we plan to investigate the influence of this triethanolammonium salt solution on the growth properties of the fungus *Rhizopus oryzae* (culture *Rhizopus oryzae* F-814), which belongs to the microorganism permitted for use in food industry.

2. Experimental

IR spectra were recorded by the Nicolet 8700 (Thermo Scientific) FTIR spectrometer. Pellets for studying IR spectra of compouds were produced by pressing in KBr. Elemental analysis was performed on Elemental analyzer Euro EA3028-NT for the simultaneous determination of C, H, N. NMR spectra in DMSO-d6 2-5% solutions were registered on a Bruker Avance III spectrometer [400.13 (^{1}H), 100.613 MHz (^{13}C)]. Chemical shifts presented below are relative to residual signals of dimethyl sulfoxide (2.50 ppm for ^{1}H and 39.52 ppm for ^{13}C) [29].

The single crystal X-ray diffraction experiment was performed on Agilent Technologies Xcalibur Eos diffractometer at 100 K using monochromated MoKα radiation. Experimental details are shown in Table 1. The structure has been solved by the direct methods and refined by means of the SHELX program [30] incorporated in the *OLEX2* program package [31]. The carbon-bound H atoms were placed in calculated positions and were included in the refinement in the ‘riding’ model approximation, with U_{iso}(H) set to 1.2U_{eq}(C) and C–H 0.97 Å for the CH_2 groups, U_{iso}(H) set to 1.5U_{eq}(C) and C–H 0.96 Å for the CH_3 groups and U_{iso}(H) set to 1.2U_{eq}(C) and C–H 0.93 Å for the CH. All H atoms bonded to N and O atoms were located in a difference Fourier map. Empirical absorption correction was applied in CrysAlisPro [32] program complex using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Supplementary crystallographic data for this paper have been deposited at Cambridge CrystallographicData Centre (CCDC 1448986) and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif

Table 1. Experimental details.

Crystal data	Triethanolammonium salicylate
Chemical formula	$C_{13}H_{21}NO_6$
M_r	287.31
Crystal system, space group	orthorhombic, $Pca2_1$
Temperature (K)	100
a, b, c (Å)	10.3205(7), 11,2445(8), 24,3654(17)
α, β, γ	90, 90, 90
V ($Å^3$)	2827.6(3)
Z	8
Radiation type	Mo Kα
μ (mm^{-1})	0.107
Crystal size (mm)	0.18 × 0.17 × 0.15
Data collection	
Diffractometer	Xcalibur, Eos diffractometer
Absorption correction	multi-scan
T_{min}, T_{max}	0.845, 1.000
No. of measured, independent and observed [$I>2\sigma(I)$] reflections	17583, 5776, 5246
R_{int}	0.025
θ_{min}- θ_{max}	3.21 - 27.50
Refinement	
$R[F^2> 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.078, 1.05
No. of reflections	5776
No. of parameters	368
No. of restraints	0
H-atom treatment	mixed
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.25, −0.22

2.1. Synthesis

1) Triethanolammonium salicylate was prepared by dropping the stoichiometric amount of methanol solution of salicylic acid (7 mmol, 0.97 g.) to the methanol solution of triethanolamine (7 mmol, 1.04 g.). The reaction mixture was stirred during 1 h at 60-65 °C. After the completion of the reaction, methanol was evaporated under the reduced pressure. The resulting product was yellowish

viscous liquid. The yield of the reaction was 99 %. The crystals were grown from the liquid phase at room temperature for a long period (over three months). The final product was washed with diethyl ether and dried *in vacuo*. Elemental analysis calculated for $C_{13}H_{21}NO_6$, %: C 54.35; H 7.37; N 4.88, found, %: C 53.32; H 7.18; N 4.80. M.p. 62-64 °C.

^{1}HNMR spectrum (DMSO-d6, δ, ppm, J, Hz): 3.25 t (6H, 5.0, 5.0, $\mathrm{HN^+{-}C\underline{H_2}{-}CH_2{-}OH}$), 3.77 t (6H, 5.0, 5.0, $\mathrm{HN^+{-}CH_2{-}C\underline{H_2}{-}OH}$), 4.5-9.4 m (5H, $\mathrm{\underline{H}N^+{-}CH_2{-}CH_2{-}O\underline{H}}$, $\mathrm{\underline{H}O{-}C_{Ar}}$), 6.64-6.72 m (2H, $\mathrm{C_{Ar}{-}H}$), 7.21 t (1H, 7.6, 7.6, $\mathrm{C_{Ar}{-}H}$), 7.71 d (1H, 7.6, $\mathrm{C_{Ar}{-}H}$)

^{13}CNMR spectrum (DMSO-d6, δ, ppm): 55.4 ($\mathrm{HN^+{-}\underline{C}H_2{-}CH_2{-}OH}$), 55.7 ($\mathrm{HN^+{-}CH_2{-}\underline{C}H_2{-}OH}$), 116.0 ($\mathrm{\underline{C}_{Ar}{-}H}$), 116.8 ($\mathrm{\underline{C}_{Ar}{-}H}$), 119.2 ($\mathrm{\underline{C}_{Ar}}$), 130.2 ($\mathrm{\underline{C}_{Ar}{-}H}$), 132.2 ($\mathrm{\underline{C}_{Ar}{-}H}$), 162.1 ($\mathrm{\underline{C}_{Ar}}$), 172.3 ($\mathrm{^-OO\underline{C}{-}\ C_{Ar}}$)

2) Silver salicylate was prepared by dropping the stoichiometric amount of ethanol solution of silver nitrate (2 mmol, 0.34 g.) to the ethanol solution of triethanolammonium salicylate (2 mmol, 0.57 g.) at stirring. The crystals of silver salicylate were precipitated from solution almost immediately.

2.3. Antifungal activity

The fungus *Rhizopus oryzae* F-814 was grown on glucose-peptone medium. The solutions of triethanolammonium salt of salicylic acid with 0,01 %, 0,001 % and 0,0001 % concentrations were introduced in the composition of the medium. The cultivation was performed for three days at 28 °C. The amount of biomass was determined by the gravimetric method. The amount of biomass in the control sample was 3.7±0.1 g/L.

3. Results and discussion

The interaction of triethanolamine (TEA) with salicylic acid leads to proton transfer from the acid to a TEA molecule, and as result the triethanolammonium cation and salicylate anion are formed. Structure of the resulting salt was established, and cation-anion interactions were investigated by X-ray diffraction analysis.

3.1. Structure and cation-anion interactions

The structure of triethanolammonium salicylate (figure 3) was determined by single crystal X-ray diffraction (XRD) analysis. In contrast to triethanolammonium 2-formylbenzoate [28] triethanolammonium cation $[(OHCH_2CH_2)_3NH]^+$ has *endo*-conformation: three oxygen atoms from CH_2CH_2OH branches surround the hydrogen atom of the NH group, with the formation of a trifurcated hydrogen bonds. The bond lengths and bond angles are listed in table 2.

Table 2. Selected geometric parameters (Ǻ, °) for triethanolammonium salicylate, the atom-numbering scheme are presented in the figure 3.

bond lengths (Ǻ)		bond angles ω (deg)	
N2-C15	1.510(2)	C35 N2 C15	111.45(15)
N2-C21	1.513(3)	C21 N2 C15	112.23(13)
N2-C35	1.510(2)	C35 N2 C21	111.77(14)
N2-H2	0.910(2)	C28 C15 N2	110.14(14)
C15-C28	1.513(2)	C30 C21 N2	111.01(14)
C28-O1	1.424(2)	C29 C35 N2	111.51(14)
C21-C30	1.508(2)	C15 C28 O1	107.00(14)
C30-O9	1.428(2)	C35 C29 O4	107.15(13)
C35-C29	1.508(2)	C21 C30 O9	107.66(13)
C29-O4	1.426(2)	O11 C24 O6	122.51(17)
C24-O6	1.264(2)	C19 C24 O6	120.15(15)
C24-O11	1.271(2)	C19 C24 O11	117.31(14)
C19-C24	1.502(3)	C19 C36 O13	120.62(16)
C36-O13	1.361(2)	C23 C36 O13	119.65(15)

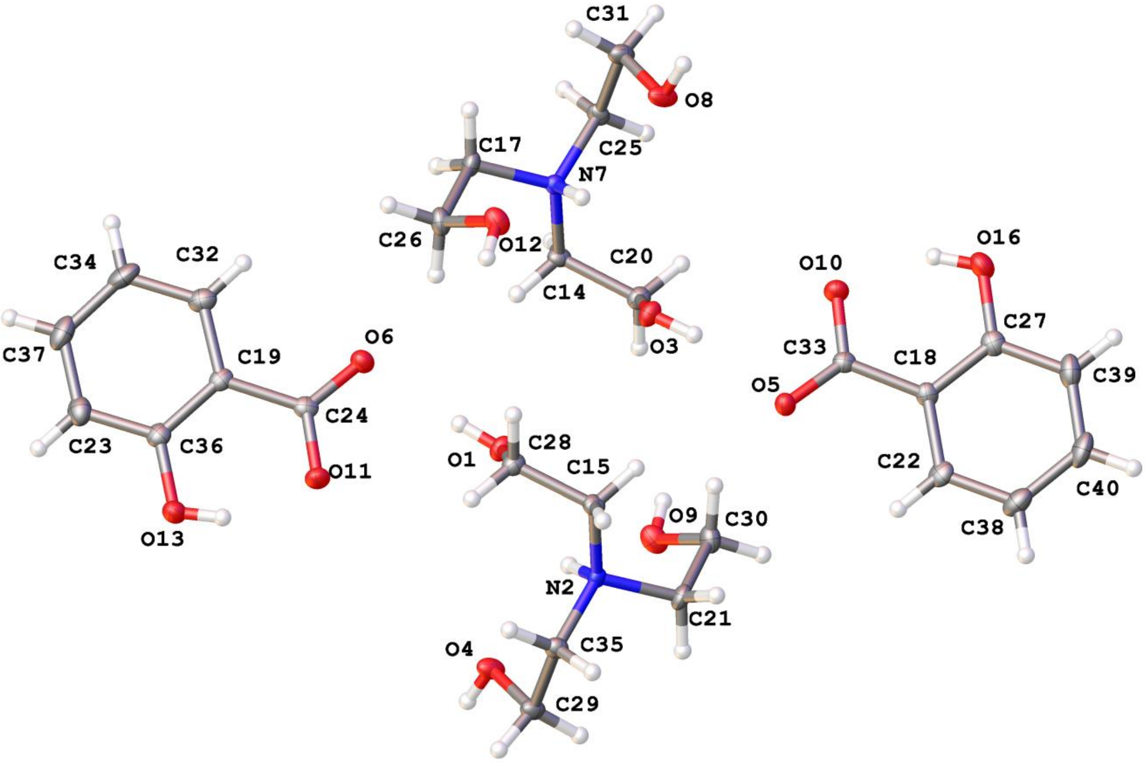

Figure 3

Cation-anion interactions. It was found by XRD analysis that triethanolammonium cation $[(OHCH_2CH_2)_3NH]^+$ are associated with COO$^-$- and OH-groups of salicylate anion by intermolecular hydrogen bonds. One oxygen atom of the anionic carboxyl group (O5) forms two intermolecular hydrogen bonds (1.882 and 1.936 Å) with OH-groups of two cations. The second oxygen atom of this carboxyl group (O10) forms the intramolecular bond with the proton of the OH group of the salicylate anion (1.742 Å). The oxygen atom of this hydroxyl group of salicylate anion acts not only as a proton donor, but also as a proton acceptor for the weaker H-bonding (2.000 Å) with the OH-group of the triethanolammonium cation (figure 4, table 3).

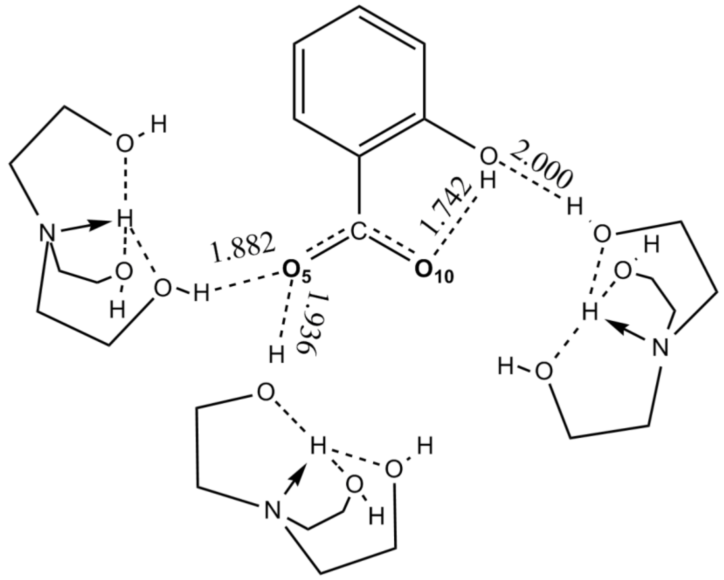

Figure 4

The molecular packing. If we consider the structure along the *a* axis, we can see that it is composed of three-layer corrugated walls lying in the *ab* plane and linking together only by van der Waals bonds. Each of the walls consists of duplicate columns of triethanolammonium $[(OHCH_2CH_2)_3NH]^+$ cations, oriented along the *a* axis. In this connection the adjacent columns are constructed of symmetrically unrelated cations, and the cations in adjacent columns are oriented antiparallel, i.e. the hydrogen atoms at the nitrogen atom – N_{am}, and hence hydroxyethyl CH_2CH_2OH branches turn in the opposite directions (Fig. 5 a).

Cations within the column do not directly interact with each other, but connect with each other and with neighboring columns within the walls by hydrogen bonds with anions of salicylic acid located on the periphery of the walls. It should be noted that there is no anion, which would be directly connect two cations located in the same column and arranged one under the other by hydrogen bonds. Anions of salicylic acid, as well as cations are not connected directly with each other, but link one cation from one column to another cation in the adjacent column. Since no symmetry related cations have different coordinate along the *a* axis, this leads to the formation of infinite walls perpendicular to the *c*-axis.

The walls are packed by “fish tail” type, which can be seen from a view along the *b* axis (Fig. 5 b). The molecular packing and the nature of intermolecular interactions in triethanolammonium salicylate are presented in figure 5 and table 3.

Table 3. Hydrogen-bond lenghts for triethanolammonium salicylate (Ǻ, deg). Atom-numbering scheme is shown in the figure 3.

D-H⋯A	**D-H**	**H⋯A**	**D⋯A**	**D-H⋯A**
O4-H4⋯O5a	0.820(8)	1.882(7)	2.699(2)	174.31(1)
O9-H9⋯O16b	0.820(6)	2.000(8)	2.802(2)	165.75(1)
O1-H1⋯O6	0.820(3)	1.943(3)	2.761(2)	175.51(2)
O13-H13⋯O11	0.819(2)	1.729(11)	2.467(2)	148.87(1)
O12-H12⋯O13c	0.820(7)	1.953(7)	2.767(2)	171.83(5)
O8-H8⋯O6a	0.820(9)	1.888(8)	2.704(1)	173.49(20)
O3-H3⋯O5	0.820(3)	1.936(5)	2.741(2)	167.10(2)

Symmetry code: a -1/2+x, -y, z; b -1/2+x, 1-y, z; c 1/2+x, -y, z

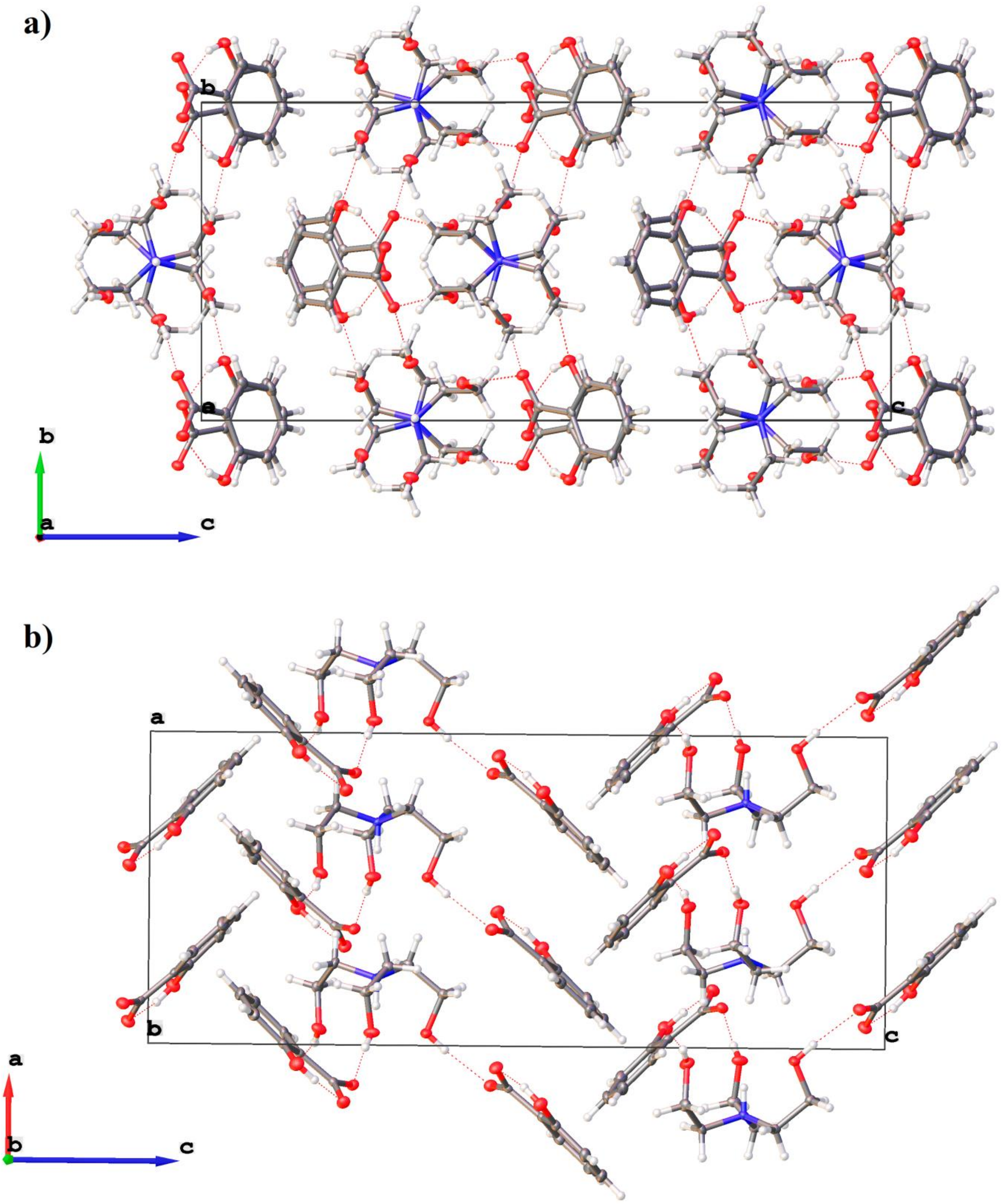

Figure 5

IR spectroscopy

Triethanolammonium salicylate was investigated by IR spectroscopy. We obtained the IR spectrum in the region of 4000-650 cm^{-1}. The following assignment of main bands is proposed.

The band at 3350 cm^{-1} belongs to stretching vibrations of OH groups of protatrane cation and the lower one at 3150 cm^{-1} to NH stretching. These bands may be overlapped by ν(OH) of the COH group involved in the intramolecular hydrogen bonding and CH stretchings of the phenyl ring. Methylene CH_2 stretching modes of protatrane are responsible for bands in the 2930-2900 cm^{-1} spectral region. Similar frequencies have bands in triethanolammonium salts formed by inorganic acids HHal (Hal = Cl, Br, J) [13]. Other vibrations of triethanolammonium cation may be assigned to CH_2 deformations (1490-1410 cm^{-1} and 1250-1140 cm^{-1}). Bands in the 1090-917 cm^{-1} region belong to CO, CN, and CC vibrations of the TEA cage [13]. The 1640 cm^{-1} and 1590 cm^{-1} bands correspond to 1652 and 1582 cm^{-1} bands in the IR spectrum of sodium salicylate assigned to ν(C=O) and ν(CC) correspondingly [33]. The 1320 and 1290 cm^{-1} bands of triethanolammonium salicylate may correspond to 1317 cm^{-1} (ν (C=O)) and 1299 cm^{-1} (ν(CC)) bands of sodium salicylate [33]. In the same region may be found deformation vibrations of the hydrogen bound COH group and phenyl ring vibrations. Thus, the only vibrations which may characterize the carboxylic group is the assymetric stretching at 1640 cm^{-1}. It lies slightly lower than the corresponding band in sodium salicylate (1652 cm^{-1}) but substantially higher than those of methyl (1682 cm^{-1}) and ethyl (1678 cm^{-1}) salicylate with asymmetric carboxyl groups [34, 35].

3.2. Interaction with $AgNO_3$

With the purpose of obtaining new silver-containing complexes, the interaction of triethanolammonium salicylate with silver (I) salts was investigated in ethanol media. According to [36, 37] the interaction of triethanolammonium salts of protic acids with transition metals salts leads to the formation of water soluble complexes with atrane structure (figure 6).

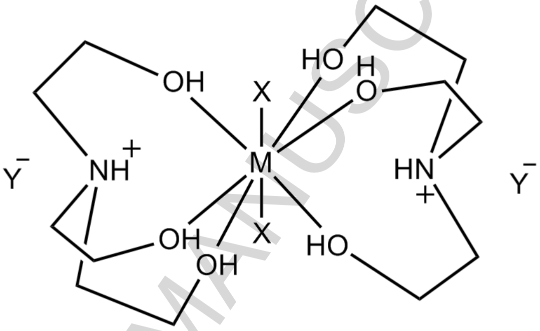

Figure 6

However, it was found experimentally that the interaction of triethanolammonium salicylate with $AgNO_3$ in the ethanol medium leads to the formation of insoluble crystalline product. X-ray diffraction analysis found that the reaction product is silver (I) salicylate of the dimeric structure (fig. 7). Similar reaction occurs with triethanolammonium salt of benzoic acid. Thus, the exchange reaction is proceeded at interaction of triethanolammonium salts with silver (I) nitrate, and insoluble organic silver (I) salts are formed. Note that the direct interaction of silver (I) salts with triethanolamine leads to the oxidation-reduction reaction in which silver ions under the action of triethanolamine are reduced to metallic silver, and CH_2CH_2OH groups of TEA are oxidized to aldehyde -CH_2CHO groups [38]. The structure of silver (I) salicylate has already been established by X-ray diffraction previously [39], therefore the detailed description of its structure is omitted here.

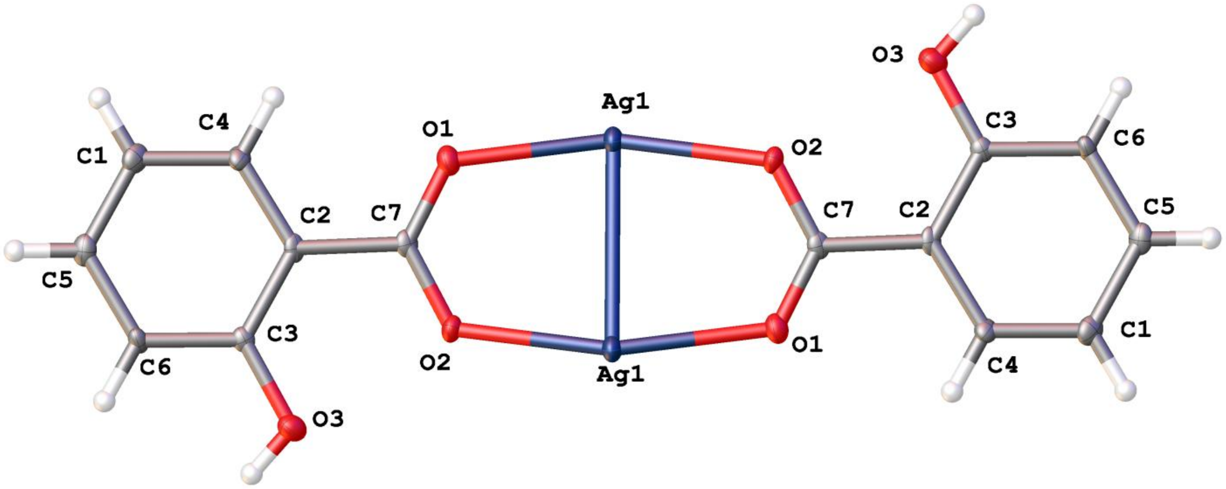

Figure 7

3.3. The influence on growth properties of the fungus Rhizopus oryzae F-814

The fungus *Rhizopus oryzae (R. oryzae)* belongs to the class of *Zygomycetes*, order of *Mucorales*, family of *Mucoraceae*. Different strains of *R. oryzae* are the producers of lactic and fumaric acids, enzymes, amylase, glucoamylase, lipase, protease, chitin deacetylase and biosorbents, which can find application in various fields [40, 41]. It is known that salicylic acid is widely used in cosmetology and medicine due to its antiseptic action. Based on the papers [14-18], it can be expected that triethanolammonium salicylate would have a similar effect. We investigated the effect of aqueous solutions of triethanolammonium salicylate on the growth properties of the fungus *Rhizopus oryzae* F-814, the results are presented in table 4.

Table 4. The amount of biomass of the fungus *R. oryzae*, g/l in the presence of solutions of triethanolammonium salicylate with 0.01%, 0.001% and 0.0001% concentration

Concentration of solution of triethanolammonium salicylate, %	0.0001	0.001	0.01
The amount of biomass of the fungus *R. oryzae*, g/l	3.8±0.1	3.5±0.1	2.9±0.1

The amount of biomass in the control sample is 3.7±0.1 g/l.

From table 4 it is seen that with increasing the concentration of solution of triethanolammonium salicylate, the amount of biomass of the fungus *R. Oryzae* is reduced. Thus, solutions of triethanolammonium salicylate inhibit the growth of this culture.

4. Conclusion

Thus, the triethanolammonium salt of salicylic acid which belongs to the class of protic alkanolammonium ionic liquids, was synthesized. The structure of triethanolammonium salicylate was established by single crystal X-ray diffraction analysis. It is shown that the cations have a protatrane structure with *endo*-configuration (the presence three trifurcated hydrogen bonds). Cations are involved in the formation of intermolecular hydrogen bonds with the oxygen of COO- and the OH-groups of salicylate anion.

Interaction of triethanolammonium salicylate with $AgNO_3$ leads to the formation of a crystalline precipitate with dimeric structure $C_{14}H_{10}Ag_2O_6$.

The influence of solutions of triethanolammonium salicylate on the growth properties of the fungus *Rhizopus oryzae* F-814 was studied. It was found that the investigated ionic liquid inhibits the growth of this culture, the greatest effect is observed when the concentration of the introduced salt is 0.01%.

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Figure Captions

Figure 1. Triethanolammonium salt of protic acid (X – anion of protic acid)

Figure 2. The structure of triethanolammonium 2-formylbenzoate [28]

Figure 3. The molecular species in triethanolammonium salicylate, with the atom-numbering scheme. H atoms are not numbered

Figure 4. Cation-anion interactions in triethanolammonium salicylate

Figure 5. The molecular packing in triethanolammonium salicylate, viewed along the a axis (a) and b axis (b). Dashed lines indicate the intermolecular hydrogen bonding

Figure 6. The structure of metal-containing complexes with atrane structure (M = Zn, Co, Ni, Mn, etc.; X = Hal, Y - the anion of carboxylic acid) [36, 37]

Figure 7. The structure of the silver (I) salicylate according to the XDA with the the atom-numbering scheme. H atoms have been omitted

Highlights

- X-ray structure of triethanolammonium (TEA) salt of salicylic acid is determined.
- $C_{14}H_{10}Ag_2O_6$ dimer is formed by the reaction of TEA salicylate with $AgNO_3$.
- Properties of fungus *Rhizopusoryzae* F-814 influenced by TEA salicylate are studied.