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СИНТЕЗ И ХАРАКТЕРИСТИКИ ПЕРФТОРЭТИЛЗАМЕЩЕННЫХ ОЛИГОФТОРФОСФАТОВ АЛКИЛАММОНИЯ

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Моно-, ди-, триперфторэтилзамещенные фторфосфат-анионы являются билдинг-блоками в молекулярном дизайне солей с ониевыми катионами и используются для повышения гидрофобности, модификации поверхностно-активных свойств и электропроводности. В работе предложены методы синтеза суперкислоты $H^+[PF_3(C_2F_5)_3]^-$ реакцией три(пентафторэтил)дифторфосфорана с раствором плавиковой кислоты, а также суперкислот $H^+[PF_4(C_2F_5)_2]^-$ и $H^+[PF_5C_2F_5]^-$ постадийным снятием перфторэтильного заместителя гидролизом с последующей обработкой раствором HF. На основе полученных суперкислот метатезисом анионов при 0 °C из соответствующего хлорида четвертичного аммония синтезированы ионные соединения из группы NR_4FAP с катионом трибутилметиламмония общей формулы $[(C_4H_9)_3NCH_3]^+[PF_{6-n}(C_2F_5)_n]^-$, где $n = 1, 2, 3$. Квадратная бипирамидальная структура трех изучаемых анионов подтверждена данными спектроскопии ядерного магнитного резонанса (ЯМР) и рентгеноструктурного анализа (РСА). Методами дифференциальной сканирующей калориметрии (ДСК) и синхронного термического анализа (СТА) показано, что синтезированные соединения характеризуются чрезвычайно низким давлением паров до 300 °C, широким диапазоном жидкого состояния шириной до 310 K и относятся к ионным жидкостям (ИЖ), в том числе одна к типу жидких при комнатной температуре (RT-IL). Определены температуры и энтальпии плавления. Методом анализа выделяющихся газов (СТА-АВГ) проанализированы общие закономерности разложения соединений, показано, что во всех случаях разложение изучаемых ионных жидкостей начинается с деструкции аниона. Изучено электросопротивление чистой ионной жидкости при комнатной температуре. Описанные характеристики перфторэтилзамещенных олигофторфосфатов алкиламмония открывают перспективы для использования их в качестве электропроводящих и антистатических добавок для нефтехимии, топлив и полимеров.

Ключевые слова: трифтор[трис(пентафторэтил)]фосфаты аммония, перфторэтилфосфоран, координационная химия, кристаллическая структура, термический анализ, электропроводность

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PREPARATION AND CHARACTERIZATION OF PERFLUOROETHYLSUBSTITUTED ALKYLAMMONIUM OLIGOFLUOROPHOSPHATES

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Mono-, di-, triperfluoroethyl substituted fluorophosphate anions are building blocks in the molecular design of salts with onium cations, and are used to increase hydrophobicity, modify surfactant properties and electrical conductivity. The work proposes methods for the synthesis of superacid $H^+[PF_3(C_2F_5)_3]^-$ by the reaction of tri(pentafluoroethyl)difluorophosphorane with a solution of hydrofluoric acid, as well as superacids $H^+[PF_4(C_2F_5)_2]^-$ and $H^+[PF_5C_2F_5]^-$ by step-by-step removal of the pentafluoroethyl substituent by hydrolysis with subsequent treatment with HF solution. Ionic compounds were synthesized by metathesis of anions at 0 °C from the corresponding quaternary ammonium chloride based on the obtained superacids. The article presents NR_4FAP-class ionic compounds with the tributylmethylammonium (TBMA) cation of the general formula $[(C_4H_9)_3NCH_3]^+[PF_{6-n}(C_2F_5)_n]^-$, where $n = 1, 2, 3$. The square bipyramidal structure of the three studied anions was confirmed by nuclear magnetic resonance (NMR) spectroscopy and X-ray diffraction (XRD) data. The study shows, the synthesized compounds are characterized by extremely low vapor pressure up to 300 °C, a wide range of the liquid state with a width of up to 310 K by the methods of differential scanning calorimetry (DSC) and synchronous thermal analysis (STA). Melting temperatures and enthalpies were determined. The TBMA salts belong to ionic liquids (IL's), including one type liquid at room temperature (RT-IL). The general patterns of compounds decomposition were analyzed by the analysis of evolved gases (STA-EGA); it was shown that in all cases, the decomposition of the studied ionic liquids begins with the destruction of the anion. The electrical resistance of a pure ionic liquid at room temperature was studied. The described characteristics of perfluoroethylsubstituted alkyl ammonium oligofluorophosphates open up prospects for their use as electro conducting and antistatic additives for petrochemicals, fuels and polymers.

Key words: ammonium trifluoro[tris(pentafluoroethyl)]phosphates, perfluoroethylphosphorane, coordination chemistry, crystal structure, thermal analysis, electrical conductivity

INTRODUCTION

Due to their unique properties, ionic liquids (with perfluoroalkylfluorophosphate anions) are demanded by different industries and have a broad range of uses. The number of research papers devoted to these compounds is increasing exponentially. Although their application field is becoming wider and wider, the development of new ionic compounds with a melting point below 100 °C is still an urgent task. The synthesis of new compounds, liquid at room temperature, so called room-temperature ionic liquids (RT-ILs), is of especial importance. As a rule, RT-ILs are highly polar, non-volatile, non-combustible, electrically and thermally conductive and low-toxic compounds [1, 2]. In addition, ILs are characterized by a high heat capacity, thermal and chemical stability, resistance to hydrolysis, complex formation ability and intermolecular interaction [3]. Due to these properties, IL can be considered to be a promising alternative to conventional organic solvents, electrolyte and reaction media, and catalysts [4-7].

It is noteworthy, that RT-ILs are widely used for reducing the triboelectric effect, for example, as antistatic additives to petrochemical products, fuels, and polymers [8-10].

Selecting the appropriate cation and/or anion, the compounds with the characteristics required for specific practical applications can be prepared. Both cations and anions can be modified to meet the requirements of a process. For example, hydrocarbon radicals can be introduced into the cation structure to achieve an affinity for non-polar media, such as mineral/synthetic oils and motor fuel. Hydrolytic and thermal stability can be improved in presence of fluorine-substituted anions [11, 12].

Taking into account all these considerations, a novel series of ILs has been developed. Present paper is devoted to preparation and study of perfluoroethylsubstituted alkylammonium oligofluorophosphates.

EXPEREMENTAL PART

All the reagents were purchased from commercial sources and used without further purification. The purity and structure of the compounds were established by NMR.

NMR spectra of the compounds were recorded using a Bruker AVANCE III HD (400 MHz) spectrometer. For the measurements, 5% DMSO-d6 solutions of the crystalline compounds were prepared. Liquid compounds were studied in pure state using a DMSO-d6 capillary.

Thermal stability and properties were studied using a Netzsch STA 449 F1 Ju-piter® thermal analyzer coupled with a QMS 403 C Aëolos® mass spectrometer and a DSC 214 Polyma calorimeter (Netzsch, Germany). The thermal curves were recorded at a heating rate of 10 K/min in a dynamic atmosphere of argon in the temperature range of 0-500 °C. The samples were placed into a platinum crucible; the calibration was carried out using the reference substances; the initial data were corrected using the software supplied by the manufacturer. The mass spectra of the degradation products were recorded in the histogram mode with the product identification according to the NIST 2008 database.

X-ray diffraction patterns were recorded using an Agilent Xcalibur Ruby single-crystal diffractometer equipped with a CCD detector (MoKα radiation, 295(2) K, ω-scanning with a step of 1°). The absorption was taken into account empirically using the SCALE3 ABSPACK algorithm. The structures were solved using the SHELXT and SUPERFLIP [13] structure solution programs and refined by full-matrix least squares on F^2 with anisotropic displacement parameters for the non-H atoms using the SHELXL program [14] with the OLEX2 graphical interface [15]. Hydrogen atoms are placed at calculated positions and refined using a riding model. The XRD data were registered in the Cambridge Crystallographic Data Center (CCDC) under the numbers 2265071 (compound ***8***) and 2265072 (compound ***9***) and can be requested at www.ccdc.cam.ac.uk/structures.

Preparation of bis(pentafluoroethyl)phosphinic acid ***2***.

213 g (0.5 mol) of tris(pentafluoroethyl)difluorophosphorane was slowly added to 65 g (4 mol) of water in a fluoroplastic flask at vigorous stirring at room temperature. The resulting solution was stirred at 40-60 °C for 30. Then aqueous HF was distilled off to 0.2% content. If necessary, the reaction mixture was distilled under reduced pressure (0.6 mbar). Liquid bis(pentafluoroethyl)phosphinic acid was obtained in a yield of 77%. The product yield was calculated taking into account the amount of tris(pentafluoroethyl)difluorophosphorane. ^{19}F NMR (377 MHz, DMSO-d6) δ -82.23 – -82.36 (m, $2CF_3$), -126.91 (d, J = 81.7 Hz, $2CF_2$). ^{31}P NMR (162 MHz, DMSO-d6) δ 3.29 (p, J = 81.9 Hz).

Preparation of pentafluoroethylphosphonic acid ***3***.

213 g (0.5 mol) of tris(pentafluoroethyl)difluorophosphorane was slowly added to 104 g (6.5 mol) of water at vigorous stirring. The resulting solution was heated and stirred at 80-90 °C for 7 days. The completeness of the reaction was monitored using ^{31}P-NMR spectroscopy. Then aqueous hydrogen fluoride solution was distilled off. The residue was dried in oil bath under reduced pressure at 60-70 °C for 10 h. Liquid pentafluoroethylphosphonic acid was obtained in a yield of 99%. The product yield was calculated taking into account the amount of tris(pentafluoroethyl)difluorophosphorane. ^{19}F NMR (377 MHz, DMSO-d6) δ -82.91 – -83.24 (m, CF_3), -128.16 (d, J = 86.6 Hz, CF_2). ^{31}P NMR (162 MHz, DMSO-d6) δ -2.53 (t, J = 87.7 Hz).

Preparation of tris(pentafluoroethyl)trifluorophosphoric acid ***4*** (***HFAP-3***).

100 g of tris(pentafluoroethyl)difluorophosphorane was introduced into a 1-L Teflon reactor, equipped with a Teflon stirrer and a funnel for adding anhydrous hydrogen fluoride. Then 50 g of anhydrous hydrogen fluoride was added at 0 °C at dry ice bath (with at least 5-10% excess). A homogeneous light-grey solution was obtained. The HFAP structure was confirmed by the NMR data. ^{19}F ЯМР (377 MHz, DMSO-d6) δ -44.09 (dm, J = 889 Hz, PF), -79.28 – -79.49 (m, CF_2), -80.67 – -81.03 (m, $2CF_2$), -87.30 (dm, J = 904.0 Hz, 2PF), -115.28 (dm, J = 83 Hz, CF_3), -115.77 (dm, J = 97 Hz, $2CF_3$). ^{31}P ЯМР (162 MHz, DMSO-d6) δ -148.23 (qseptm J = 904 Hz, J = 97 Hz).

Preparation of bis(pentafluoroethyl)tetrafluorophosphoric acid ***5*** (***HFAP-2***).

A 1-L Teflon reactor, equipped with a Teflon stirrer and a funnel for adding anhydrous hydrogen fluoride, was charged with 100 g of bis(pentafluoroethyl)phosphinic acid (main substance content 93%, moisture content 20%). Then 50 g of anhydrous hydrogen fluoride was added at vigorous stirring at 0 °C. A homogeneous light-grey solution was obtained.^{19}F NMR (377 MHz, DMSO-d6) δ -75.22 (dm, J = 937.92, PF4), -85.66 – -85.77 (m, CF_3), -121.14 (dm, J = 109.31Hz, CF_2). ^{31}P NMR (162 MHz, DMSO-d6) δ -147.08 (pp, J =938.54, 109.81 Hz).

Preparation of pentafluoroethylpentafluorophosphoric acid ***6*** (**HFAP-1**).

A 1-L Teflon reactor, equipped with a Teflon stirrer and a funnel for adding anhydrous hydrogen fluoride, was charged with 100 g of pentafluoroethylphosphonic acid and cooled in ice-bath. Then 50 g of anhydrous hydrogen fluoride was added at vigorous stirring at 0 °C. A homogeneous grey solution was obtained. ^{19}F NMR (377 MHz, DMSO-d_6) δ -71.28 (dh, J = 826.5, 8.2 Hz, 2PF), -74.72 (dp, J = 722.6, 49.1, 47.6 Hz, 3PF), -83.64 (pd, J = 7.8, 2.9 Hz, CF_3), -119.99 (dp, J = 89.8, 9.0 Hz, CF_2). ^{31}P NMR (162 MHz, DMSO-d_6) δ -148.17 (pp, J =826.5, 722.6, 104.0, 89.8, 2.9 Hz).

Preparation of tributylmethylammonium tris(pentafluoroethyl)trifluorophosphate ***7*** **(TBMA-3)**.

40 ml of ice water was added to 151 g of tris(perfluoroethyl)trifluorophosphoric acid (HFAP-3) at stirring at 0 °C. Then 80 g of tributylmethylammonium chloride solution in 100 ml of deionized water was added. A thick light-grey precipitate quickly settled down. The mixture was stirred at 0 °C for 45 min, then 50 ml of water was added and the reaction mixture was kept for 40 min until room temperature (20 °C) was achieved. The precipitate was filtered on a Buchner funnel and washed six times with 50 ml of ice water to pH = 4-5. The product, a viscous colorless liquid, was obtained in a yield of 95%. The product had the following characteristics: m.p. = 14 °C; $T_{decomp.}$ = 326 °C; η =792 mPa·s at 20 °C; active electrical resistance - $5.7\cdot10^{-3}$Ω. ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.24 – 3.15 (m, 6H), 2.94 (s, 3H), 1.61 (m, J = 11.9, 8.1, 6.0 Hz, 6H), 1.32 (m, J = 7.4 Hz, 6H), 0.94 (t, 9H). ^{19}F NMR (376 MHz, DMSO-d6) δ -42.61 – -45.67 (dm, PF), -79.38 – -79.67 (m, CF_3), -81.10 (m, J = 14.2, 6.5 Hz, $2CF_3$), -85.79 – -88.69 (dm, 2PF), -115.13 – -116.30 (m, 3CF2). ^{31}P NMR (162 MHz, DMSO-d_6) δ -137.57 – -158.58 (m).

Preparation of tributylmethylammonium bis(perfluoroethyl)tetrafluorophosphate ***8*** (**TBMA-2**).

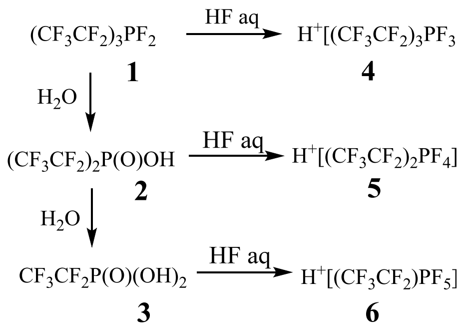
40 ml of ice-cold water was added to 118 g of bis(perfluoroethyl)tetrafluorophosphoric acid (HFAP-2) at 0 °C. Then the solution of 80 g of tributylmethylammonium chloride in 100 ml of deionized water was introduced into the reactor at stirring. A thick light-grey precipitate quickly settled down. The mixture was stirred at 0 °C for 45 min, then 50 ml of water was added and the reaction mixture was kept for 40 min until room temperature (20 °C) was achieved. The precipitate was filtered on a Buchner funnel and washed six times with 50 ml of ice water to pH = 4-5, vacuum dried. A transparent white product was obtained in a yield of 87%. The product had the following characteristics: m.p. = 66 °C; melting enthalpy λ = 53 J/g. $T_{decomp.}$ = 383 °C. Crystal structure - monoclinic syngony, space group $P2_1/n$, $C_4F_{14}P\cdot C_{13}H_{30}N$, *M* 545.39, *a* 11.875(2) Å, *b* 16.652(4) Å, *c* 12.592(3) Å, β 90.96(2)°, *V* 2489.5(10) Å^3, *Z* 4, d_{calc} 1.455 g/cm^3, μ 0.219 mm^{-1}. Final refinement parameters: R_1 0.0663 [for 2914 reflections with $I > 2\sigma(I)$], wR_2 0.2208 (for all 5834 independent reflections, R_{int} 0.0314), *S* 1.024. ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.19 – 3.13 (m, 2H), 2.97 (s, 3H), 1.73 – 1.60 (m, 3H), 1.38 (h, J = 7.4 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H). ^{19}F NMR (377 MHz, DMSO-d_6) δ -72.82 (dm, J = 16.7, 9.1, 9.0, 8.0, 7.9, 7.2 Hz), -83.47 (p, J = 7.5, 7.1 Hz), -119.95 – -120.38 (m), -120.17 (dp, J = 100.8, 9.3 Hz). ^{31}P NMR (162 MHz, DMSO-d_6) δ -149.62 (pp, J = 918.5, 914.6, 103.5, 102.1, 101.3, 100.8, 100.2, 98.9 Hz).

Preparation of tributylmethylammonium perfluoroethylpentafluorophosphate ***9*** (**TBMA-1**).

40 ml of ice-cold water was added to 83 g of mono(perfluoroethyl)pentafluorophosphoric acid (HFAP-1) at 0°. Then the solution 80 g of tributylmethyl-ammonium chloride in 100 ml of deionized water was introduced into the reactor at stirring. A thick light-grey precipitate quickly settled down. The mixture was stirred at 0 °C for 45 min, then 50 ml of water was added and the reaction mixture was kept for 40 min until room temperature (20 °C) was achieved. The precipitate was filtered on a Buchner funnel and washed six times with 50 ml of ice water to pH = 4-5. A light-grey (close to white) product yielded of 79%. The product had the following characteristics: m.p. = 69 °C; enthalpy of melting λ = 33 J/g; $T_{decomp.}$ = 330 °C. Crystal structure: rhombic system, space group *P*bca, $C_2F_{10}P\cdot C_{13}H_{30}N$, *M* 445.37, *a* 18.943(7) Å, *b* 10.476(3) Å, *c* 22.803(10) Å, *V* 4525(3) Å^3, *Z* 8, $d_{выч}$ 1.307 г/см^3, μ 0.201 мм$^{-1}$. Final refinement parameters: R_1 0.1263 [for 1337 reflections with $I > 2\sigma(I)$], wR_2 0.4681 (for all 5644 independent reflection, R_{int} 0.0762), *S* 1.015. ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.16 (d, J = 12.6 Hz, 2H), 2.90 (s, 1H), 2.34 (s, 2H), 1.97 (p, J = 2.5 Hz, 0H), 1.67 (p, J = 8.4, 7.9, 7.5 Hz, 1H), 1.38 (h, J = 7.4 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H). ^{19}F NMR (377 MHz, DMSO-d_6) δ -71.28 (dh, J = 826.5, 8.2 Hz), -74.72 (dp, J = 722.6, 49.1, 47.6 Hz), -83.64 (pd, J = 7.8, 2.9 Hz), -119.99 (dp, J = 89.8, 9.0 Hz). ^{31}P NMR (162 MHz, DMSO-d_6) δ -148.17 (pp, J =826.5, 722.6, 104.0, 89.8, 2.9 Hz).

RESULTS AND DISCUSSION

Tri(pentafluoroethyl)difluorophosphorane ***1*** is used as an initial compound for the synthesis of superacids ***4-6*** according to Scheme 1. At the first step, the initial compound is hydrolyzed to give acids ***2-3***, then fluorinated by HF solution, and used futher to get target products by anion metathesis.



Scheme 1. Synthesis of superacids ***4-6*** from tri(pentafluoroethyl)difluorophosphorane

Схема 1. Синтез суперкислот ***4-6*** из три(пентафторэтил)дифторфосфорана

Tri(pentafluoroethyl)difluorophosphoranes readily react with both organic and inorganic fluorides [16, 17]. As a rule, in industry phosphorane is obtained by electrochemical fluorination of triethylphosphine in anhydrous hydrogen fluoride according to the Simons process [18]. Phosphorane is a liquid with a boiling point of 91-92 °C. Due to its high Lewis acidity, it can be used as a catalyst in, for example, Diels-Alder reactions and Michael additives. Tri(perfluoroethyl)trifluorophosphate salts are obtained via fluoride-ion elimination from the fluorides of the main group elements subjected to phosphorane. In ice water, it slowly hydrolyzes, releasing HF. [18]

Bis(perfluoroalkyl)phosphinic acids are known for a long time and used in the production of various chemicals. In literature, a number of preparation methods for these acids is described. For example, this acids can be synthesized via the reaction of Grignard reagents with phosphoryl chloride in ether followed by quenching with water [19], or via the interaction of tri(pentafluoroethyl)difluorophosphoranes with hexamethyldisiloxane, followed by hydrolysis of the corresponding phosphine oxide [20]. The disadvantages of the latter method are the need for precise temperature control and low yields of the target acid. In addition, Ignatiev et al suggested a low-cost preparation method for bis(perfluoroethyl)phosphinic acids, described in the patents DE102008035174 and WO2003087110. The acid was obtained by direct hydrolysis of tri(pentafluoroethyl)difluorophosphoranes in high yields. In present study, the corresponding acid ***2*** was synthesized according to this method. Bis(perfluoroalkyl)phosphinic acid salts can be isolated by neutralizing the acid.

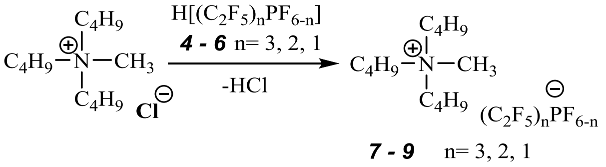
Perflouroalkylphosphonic acids are also described previously. As a rule, perflouroalkylphosphonic acids are still synthesized according to the versions of the procedure, suggested by Emeleus et al. In [20], Shreve and Mahmoud used their version of this synthetic method for preparation of compound ***3***. Hossein et al reported on a new convenient one-pot synthesis method for preparation of (perfluoroalkyl)phosphonic acid in high yield [21]. In addition, these acids can be obtained by the Ignatiev method [18].

Acids ***2*** and ***3*** were prepared according to the described above methods based on the hydrolysis of tris(pentafluoroethyl)difluorophosphorane **1**. The resulting acids were purified by distillation under reduced pressure.

Tri(pentafluoroethyl)difluorophosphorane ***1***, bis(perfluoroethyl)phosphinic acid ***2***, and pentafluoroethylphosphonic acid ***3*** are convenient reagents for the preparation of ***HFAP-3,2,1*** perfluoroethyl-substituted fluorophosphoric superacids ***4-6***. In [18], some procedures for preparation of tris(perfluoroethyl)trifluorophosphoric acid (HFAP-3) are described. Tri(perfluoroethyl)trifluorophosphoric acid can be easily obtained by reacting tri(perfluoroethyl)difluorophosphorane with hydrogen fluoride in different solvents (alcohols, dialkyl ethers, or other proton-solvating solvents) [18]. The reaction of $(C_2F_5)_3PF_2$ with aqueous HF is completed in a few minutes giving HFAP pentahydrate in stoichiometric quantity. An aqueous solution of tri(perfluoroethyl)trifluorophosphoric acid is stable at room temperature for a long time, and HFAP is a convenient initial compound for the preparation of various metal salts and ionic liquids with the FAP anion [18].

Tris(pentafluoroethyl)trifluorophosphoric (***HFAP-3***) ***4***, bis(perfluoroethyl)tetrafluorophosphoric (***HFAP-2***) ***5*** perfluoroethylpentafluorphosphoric (***HFAP-1***) ***6*** acids were prepared similar to the procedures described in patents WO2016074757-A1 and WO2005 049628-A1, via reaction of aqueous HF with tri(pentafluoroethyl)difluorophosphorane, bis(pentafluoroethyl)phosphinic and pentafluoroethylphosphonic acids, respectively.

Tributylmethylammonium pentafluoroethyl phosphates (***TBMA***) ***7, 8, 9*** were prepared by the anion metathesis reaction without isolation of acids 4-6, according to Scheme 2. After the process was completed, the reaction mixture contained the corresponding substituted ammonium fluorophosphate and an aqueous phase containing HCl. The target products are insoluble in water, well soluble in acetone, dioxane, DMSO, and DMF. The product yield was 79-95%.



Scheme 2. Synthesis of tributylmethylammonium pentafluoroethylphosphates

Схема 2 Синтез пентафторэтилфосфатов трибутилметиламмония

Compound ***7*** is a liquid at room temperature. The crystalline structure of compounds ***8***, ***9*** were first characterized by XRD. The XRD data were obtained for the single crystals of compounds ***8***, ***9***. The structures of the compounds are shown in Fig. 1 and 2.

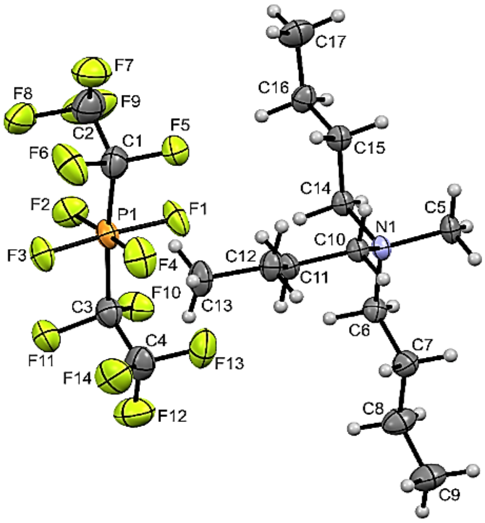


Fig. 1. The structure of tributylmethylammonium perfluoroethylpentafluorphosphate **8** according to X-ray diffraction data in thermal ellipsoids of 20% probability

Рис. 1 Структура трибутилметиламмония тетракисфторди(пентафторэтил)фосфата **8** по данным РСА в тепловых эллипсоидах 20% вероятности

The compounds ***8, 9*** crystallize in centrosymmetric space groups of orthorhombic and monoclinic crystal systems, respectively. In both cases, the crystallographically independent part of the unit cell consists of a cation and anion. In the ***TBMA-2*** compound, the anion perfluoroethyl groups are in the trans-positions. The atoms of ***TBMA-2*** anion, with the exception of the phosphorus atom, are disordered over the two positions (in Fig. 1 and 2 minor disorder components are omitted for clarity). In compound ***9*** ***(TBMA-1)***, the butyl substituents of the cation are also disordered over the two positions.

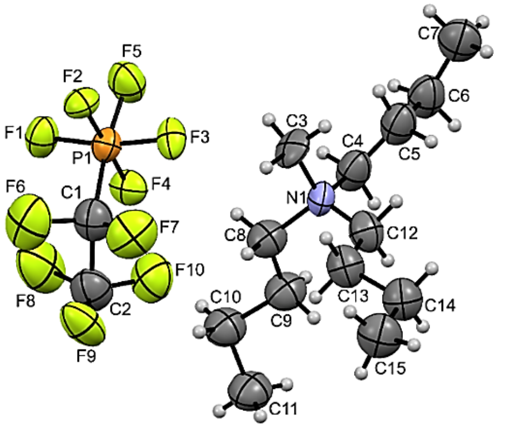
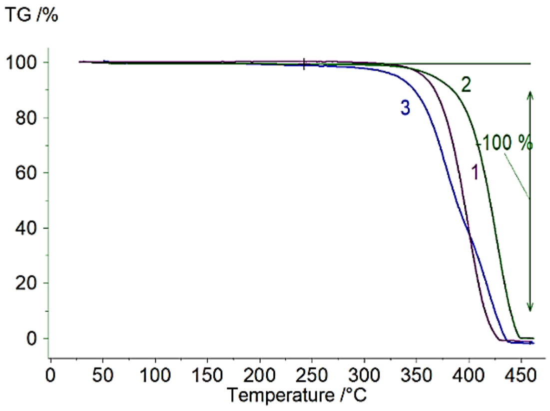
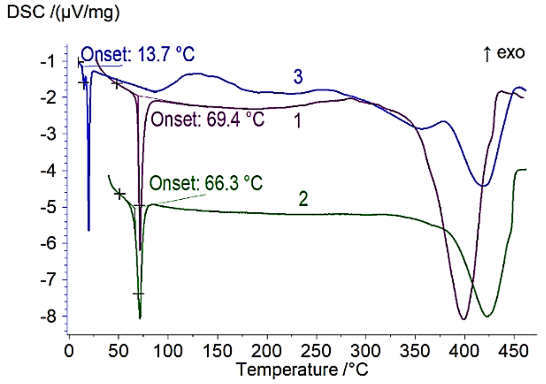


Fig. 2. The structure of tributylmethylammonium pentafluoro(perfluoroethyl)phosphate **9** according to X-ray dif-fraction data in thermal ellipsoids of 20% probability

Рис. 2. Структура пентакисфтор(пентафторэтил)фосфата трибутилметиламмония **9** по данным РСА в тепловых эллипсоидах 20% вероятности



a



b

Fig. 3a. TG analysis curves for compounds TBMA-3 (curve **3**), TBMA-2 (curve **2**), TBMA-1 (curve **1**)

Fig. 3b. DSC analysis curves for compounds TBMA-3 (curve **3**), TBMA-2 (curve **2**), TBMA-1 (curve **1**)

Рис. 3а. Результаты термогравиметрического анализа соединений TBMA-3 (кривая **3**), TBMA-2 (кривая **2**), TBMA-1 (кривая **1**)

Рис. 3б. Результаты дифференциальной сканирующей калориметрии соединений TBMA-3 (кривая **3**), TBMA-2 (кривая **2**), TBMA-1 (кривая **1**)

Compounds ***7*, *8*, *9*** were studied by simultaneous thermal analysis. As a result, the melting points were found and thermal stability of the compounds was evaluated. In addition, the general decomposition patterns of the final products were analyzed. The simultaneous thermal analysis TG curves are shown in Fig. 3a, DSC curves are shown in Fig. 3b.

Compound ***7*** (***TBMA-3***) is a viscous liquid, melting at 14°C. Dynamic viscosity at 20 °C – η = = 792 mPa·s. Active electrical resistance is $5.7\cdot10^{-3}$ Ω. In an inert atmosphere, the sample begins to decompose at the temperature above 326 °C. According to mass spectrometry data for evolved gases, thermal degradation begins with the anion cleavage. The weight loss occurs in two stages.

The melting point of compound ***8*** (***TBMA-2***) is 66 °C (ΔH = 53 J/g), compound ***9*** (***TBMA-1***) is 69 °C (ΔH = 33 J/g). The samples begin to decompose at 330-334 °C and, according to MS-EGA, the degradation begins with the anion cleavage. At the temperatures above 380 °C, a joint degradation of the ions takes place.

For the salts studied, the thermogravimetric analysis data indicate the saturated vapor pressure of the melts to be extremely low. It is interesting to note, that in an air atmosphere, the degradation temperatures of the samples decrease by 30-40 °C. In addition, the oxidative degradation is accompanied by a significant exothermic effect. Thus, the compounds are thermally stable, can be used in technology as an additives.

CONCLUSION

A synthetic route for preparation of fluorosubstituted ammonium phosphates was suggested. These compounds can be used to improve the properties of oils, polymers, and other related products. The product characteristics, in particular, an extremely high electrical conductivity allow the synthesized RT-IL to be recommended as electroconducting and electrostatic additives.

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The authors declare the absence a conflict of interest warranting disclosure in this article.

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