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ORIGINAL PAPER

Preparation of quaternary pyridinium salts as possible proton conductors

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On basis of earlier experimental experience, the transfer of protons in salts of the organic cation–inorganic anion type occurs primarily through directional arrangement of the anion–anion type short hydrogen bonds. The submitted work presents the preparation of quaternary pyridinium salts of inorganic hydrogen anions in the absence of solvent molecules in their crystal structure. These substances can form only the above-described anion–anion type hydrogen bonds; in addition, the absence of solvate anions increases the stability of the prepared compounds. A total of six substituted pyridinium salts were prepared, four of which have not been described yet: 1,2,4,6-tetraphenylpyridinium perchlorate, 1-benzyl-2,4,6-trimethylpyridinium perchlorate, 1,4-dimethylpyridinium hydrogen sulphate, 1,4-dimethylpyridinium dihydrogen phosphate, 1,4-dimethylpyridinium hydrogen sulphate, and 1,2-dimethyl-5-ethylpyridinium dihydrogen phosphate. Three of these substances were characterised by X-ray structural analysis: 1,2,4,6-tetraphenylpyridinium perchlorate crystallises in the orthorhombic system, space group Pbca; 1-benzyl-2,4,6-trimethylpyridinium perchlorate crystallises in the monoclinic system, space group $P2_1/c$; and 1,4-dimethylpyridinium dihydrogen phosphate crystallises in the monoclinic system, space group C2/c. This structure contains an oriented anion network bond by short anion–anion type hydrogen bonds with the donor acceptor lengths of 2.567(3) Å and 2.557(3) Å and thus fulfils the requirements of a good proton conductor.

Keywords: quaternary pyridinium salts, synthesis, structural analysis, hydrogen bonding and proton conductivity

Introduction

Recently, proton conductors have been greatly in demand as materials with a wide range of technical applications. In addition to being used as materials for proton-exchange membranes (Li et al., 2008) in low-temperature fuel cells or in solid oxide fuel cells (Mehta & Cooper, 2003), they are also used in other branches as potentiometric sensors for hydrogen, for gaseous mixtures analysis, or as high-temperature sensors for alkanes and alcohols. Although materials of the "nafion" type (Rikukawa & Sanui, 2000) are most frequently used on an industrial scale, the study of compounds exhibiting these properties has a fixed place in basic research as these substances can become a part of hybrid materials, where they will find practical use in the future. Here, we would like to mention crystal structures with proton conductivity, synthesised and studied at the Department of Inorganic Chemistry, Faculty of Science, Charles University in Prague. Němec et al. (2004) studied three phases of aminoguanidinium dihydrogen phosphate, whose structure contains chains of dihydrogen phosphate anions con-

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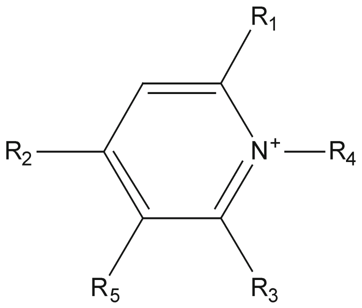

Fig. 1. General formula of the quaternary bases of interest.

nected by short hydrogen bonds with lengths between 2.496–2.521 Å. The proton exhibits proton conductivity in the direction of these chains. In the work of Smrčok et al. (2009), a crystal of 1,4-diazabicyclo[2.2.2]octane-1,4-diium dihydrogen phosphate monohydrate was studied in which, while it forms a spatial network of various types of hydrogen bonds, the proton conductivity in the direction of channels formed of dihydrogen phosphate anions connected by hydrogen bonds with lengths of 2.424 Å and 2.425 Å can be observed. In another study (Kaman et al., 2011), the base (diazabicyclooctane) was quaternized on the nitrogen atoms, excluding thus the incorporation of cations in the hydrogen bond system. In addition, the compound formed, 1,4-dimethyl-1,4-diazabicyclo[2.2.2]octane-1,4-diium hydrogen sulphate, did not contain water originating from crystallisation. The crystal structure obtained in this way contains chains of hydrogen sulphate anions connected by hydrogen bonds with lengths of 2.575 Å and 2.594 Å. However, proton conductivity of the crystal has not yet been measured.

It is apparent from these results that the hydrogen anions mutually connected in fibres, chains, or channels are the most promising structural motifs providing for proton conductivity in these structures. Thus, an acidic salt of an inorganic acid and base with quaternary nitrogen that does not contain water from crystallisation is desired. Urban and Volke (1994) were concerned with the preparation of the salts of these quaternary bases, synthesising mainly perchlorates of cations with the general formula shown in Fig. 1, and studying their electrochemical properties (Volke et al., 1992).

Although the perchlorates of these cations cannot exhibit proton conductivity because of the absence of hydrogen bonds, this work describes two so-far unpublished crystal structures of such cation salts, where $R_1 = R_2 = R_3 = R_4 = C_6H_5$ and $R_5 = H$ (1,2,4,6-tetraphenylpyridinium perchlorate), and $R_1 = R_2 = R_3 = CH_3$, $R_4 = CH_2C_6H_5$, and $R_5 = H$ (1-benzyl-2,4,6-trimethylpyridinium perchlorate). However, hydrogen salts of these cations have not been synthesised. The submitted work is concerned with the preparation of four so-far not described hydrogen salts of cations, where $R_1 = R_3 = R_5 = H$, $R_2 = R_4 = CH_3$ (1,4-dimethylpyridinium), and $R_1 = R_4 = CH_3$, $R_2 = R_3 = H$, and $R_5 = C_2H_5$ (1,2-dimethyl-5-ethylpyridinium).

Experimental

Chemical synthesis and analysis: quaternary pyridinium salts were prepared by alkylation or benzylation of commercially available pyridines: 4-methylpyridine (Aldrich), 5-ethyl-2-methylpyridine (Aldrich), and 2,4,6-trimethylpyridine (Fluka). Alkylation or benzylation was performed using methyl iodide or benzyl bromide (Fluka). Pyridinium iodides and bromides were transferred to hydroxides by freshly prepared silver oxide (from $AgNO_3$, Penta) and hydroxides solutions were neutralised using the relevant acids.

Elemental analyses were performed on a Perkin–Elmer CHNS/O 2400 instrument. ^{1}H NMR spectra were obtained with a Varian Mercury Plus 300 instrument (299.939 MHz for ^{1}H) in D_2O. Chemical shifts are given in the δ-scale. *t*-Butanol was used as the internal standard. FTIR spectra were measured in KBr on a Magna 760 Nicolet instrument. MAS spectra were measured on an Esquire 3000 (Bruker) instrument using the ESI technique.

1,4-Dimethylpyridinium iodide: methyl iodide (29.64 g, 0.21 mol) and 4-methylpyridine (18.38 g, 0.15 mol) were dissolved in 20 mL of ether. The solution was heated to 45 °C for 3 h. After cooling, the product was filtered off, washed with ether, and dried (48 g, 96 %). The product was crystallised from methanol.

1,2-Dimethyl-5-ethylpyridinium iodide was prepared from 36.48 g (0.26 mol) of methyl iodide and 29.41 g (0.24 mol) of 5-ethyl-2-methylpyridine. The reaction afforded 57 g (81 %) of the product, which was crystallised from methanol.

1-Benzyl-4-methylpyridinium bromide was prepared from 4 g (0.043 mol) of 4-methylpyridine and 6.5 g (0.038 mol) of benzyl bromide. The reaction afforded 7.3 g (73 %) of the product, which was crystallised from methanol.

1-Benzyl-5-ethyl-2-methylpyridinium bromide was prepared from 12 g (0.099 mol) of 5-ethyl-2-methylpyridine and 20 g (0.117 mol) of benzyl bromide. The reaction afforded 16.2 g (54 %) of the product, which was crystallised from methanol.

General preparation procedure for pyridinium hydroxides: halogenides were dissolved in water and excess Ag_2O was added. The mixture was stirred for 3 h. Silver halogenides and unreacted silver oxide were filtered out and the solution was titrated using H_2SO_4 over phenolphthalein to determine the hydroxide concentration. The presence and purity of the desired cations in the solutions were controlled by mass spectroscopy.

Table 1. Characterisation data of newly prepared compounds

Compound	Formula	M_r	w_i(calc.)/mass % w_i(found)/mass %			Remarks
			C	H	N	
I	$C_7H_{11}NO_4S$	204.15	41.18	5.43	6.86	contains moisture; molar ratio C : N = 6.96 (7.00 calc.)
			38.18	6.31	6.40	
II	$C_7H_{12}NO_4P$	205.15	40.99	5.89	6.82	contains moisture; molar ratio C : N = 7.00 (7.00 calc.)
			37.73	6.11	6.29	
III	$C_9H_{15}NO_4S$	233.28	46.33	6.48	6.00	contains moisture; molar ratio C : N = 8.93 (9.00 calc.)
			42.39	7.21	5.54	
IV	$C_9H_{16}NO_4P$	233.20	46.36	6.92	6.01	contains moisture; molar ratio C : N = 9.14 (9.00 calc.)
			40.35	7.73	5.15	

Table 2. Spectral data of newly prepared compounds

Compound	Spectral data
I	IR (KBr), $\tilde{\nu}$/cm^{-1}: 3381 (s), 3041 (m), 1712 (w), 1627 (s), 1589 (w), 1573 (m), 1486 (m), 1187 (s), 1063 (m) ^{1}H NMR (D_2O), δ: 2.64 (s, 3H, CH_3—Ar), 4.31 (s, 3H, CH_3—N), 7.85 (d, 2H, J = 6.3 Hz, H-3,5), 8.58 (d, 2H, J = 6.3 Hz, H-2,6)
II	IR (KBr), $\tilde{\nu}$/cm^{-1}: 3427 (s), 3039 (s), 1644 (s), 1577 (w), 1521 (m), 1479 (m), 1293 (m), 1187 (s), 1107 (w), 1042 (w), 920 (w), 825 (m), 701 (m), 545 (m), 488 (s) ^{1}H NMR (D_2O), δ: 2.64 (s, 3H, CH_3—Ar), 4.30 (s, 3H, CH_3—N), 7.84 (d, 2H, J = 6.3 Hz, H-3,5), 8.57 (d, 2H, J = 6.3 Hz, H-2,6)
III	IR (KBr), $\tilde{\nu}$/cm^{-1}: 3478 (s), 1643 (m), 1583 (w), 1532 (s), 1462 (m), 1385 (w), 1238 (s), 1050 (m), 1009 (w), 896 (m), 857 (m), 754 (w) ^{1}H NMR (D_2O) δ: 1.25 (t, 3H, J = 7.8 Hz, CH_3CH_2—Ar), 2.73 (s, 3H, CH_3—Ar), 2.79 (q, 2H, J = 7.8 Hz, CH_3CH_2—Ar), 4.19 (s, 3H, CH_3—Ar), 7.78 (d, 1H, J = 8.39 Hz, H-3), 8.22 (d, 1H, J = 8.39 Hz, H-4), 8.53 (s, 1H, H-6)
IV	IR (KBr), $\tilde{\nu}$/cm^{-1}: 3427 (s), 2973 (w), 1637 (m), 1578 (m), 1530 (s), 1289 (m), 1089 (w), 1062 (w), 1041 (w), 910 (w), 857 (w), 548 (m), 439 (m) ^{1}H NMR (D_2O), δ: 1.25 (t, 3H, J = 7.81 Hz, CH_3CH_2—Ar), 2.73 (s, 3H, CH_3—Ar), 2.79 (q, 2H, J = 7.81 Hz, CH_3CH_2—Ar), 4.18 (s, 3H, CH_3—N), 7.77 (d, 1H, J = 8.39 Hz, H-3), 8.22 (d, 1H, J = 8.39 Hz, H-4), 8.52 (s, 1H, H-6)

1,4-Dimethylpyridinium hydrogen sulphate (*I*): the solution of relevant hydroxides of known concentration was neutralised by 10 mL of H_2SO_4 (0.3 M), molar ratio 1 : 1. The solution was concentrated to 5 mL and left to crystallise over H_2SO_4. Hygroscopic crystalline powder was washed with ether.

1,4-Dimethylpyridinium dihydrogen phosphate (*II*), 1,2-dimethyl-5-ethylpyridinium hydrogen sulphate (*III*), and 1,2-dimethyl-5-ethylpyridinium dihydrogen phosphate (*IV*) were prepared by the neutralisation of relevant hydroxides by sulphuric or phosphoric acid in the molar ratio 1 : 1.

X-ray analysis of single crystals: primary data were measured on a Nonius Kappa CCD four-circle diffractometer. Radiation from the molybdenum lamp was modified using a graphite monochromator. The measurement was controlled by the Collect (Hooft, 1998) and Denzo (Otwinowski & Minor, 1997) sets of programs and was performed at the temperature of 150 K. The phase problem was resolved using direct methods by the SIR 97 program (Altomare et al., 1997). The data obtained were treated and refined by the least squares method using the SHELX 97 program (Sheldrick, 1997) with function F2 minimisation and the Platon program (Spek, 1999). Hydrogen atoms in 1,4-dimethylpyridinium dihydrogen phosphate on the oxygen atoms were found, hydrogen atoms bond to carbon atoms were located in the calculated positions. In case of 1,2,4,6-tetraphenylpyridinium perchlorate and 1-benzyl-2,4,6-trimethylpyridinium perchlorate, all hydrogen atoms (bond to carbons) were located in the calculated positions. Basic crystallographic data, data collection, and refinement parameters for all three compounds are given in Table 3. Crystallographic data for 1,2,4,6-tetraphenylpyridinium perchlorate, 1-benzyl-2,4,6-trimethylpyridinium perchlorate, and 1,4-dimethylpyridinium dihydrogen phosphate have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 898066, CCDC 898065, and CCDC 898067, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CG21EZ, UK (fax: +441223 336 031; e-mail: deposit@ccdc.cam.ac.uk).

Table 3. Experimental data for single-crystal X-ray diffraction studies of the compounds studied

Compound	1,2,4,6-Tetraphenylpyridinium perchlorate	1-Benzyl-2,4,6-trimethylpyridinium perchlorate	*IV*
Formula	$C_{29}H_{22}NClO_4$	$C_{15}H_{18}NClO_4$	$C_7H_{12}NO_4P$
Formula mass	483.93	311.75	205.15
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Pbca	$P2_1/c$	C2/c
a/Å	16.3580(3)	9.7753(4)	15.8940(4)
b/Å	16.5530(3)	12.0300(4)	16.1480(3)
c/Å	17.5080(3)	14.4020(6)	7.5850(1)
α/°	90	90	90
β/°	90	116.528(2)	108.429(10)
γ/°	90	90	90
V/Å^3	4710.71(15)	1515.32(11)	1846.90(6)
Z	8	4	8
$D_{\text{(calc)}}/(\text{g mL}^{-1})$	1.356	1.367	1.476
$\mu_{(\text{MoK}\alpha)}/\text{mm}^{-1}$	0.198	0.267	0.281
$F_{(000)}$	2016	656	864
Crystal size/mm	0.30 × 0.30 × 0.10	0.20 × 0.27 × 0.40	0.12 × 0.22 × 0.40
Radiation/Å	0.71073	0.71073	0.71073
θ/° (min–max)	2.1–27.47	3.42–27.47	1.85–27.52
Index ranges	–21,21; –21,21; –22,22	–12,12; –15,15; –18,18	–20,20; 20,20; 9,9
Number of reflections measured/unique/observed	10282/5424/4076	6377/3458/2359	4164/2119/1891
Data/restrains/parameters	5424/0/338	3458/0/221	2119/0/128
Goodness-of-fit on F^2	1.114	1.027	1.070
Final R, $R_{\text{(alldata)}}$	0.0450, 0.0686	0.0446, 0.0786	0.0290, 0.0370
Largest difference of peak and hole	0.340, –0.668	0.291, –0.331	0.412, –0.474

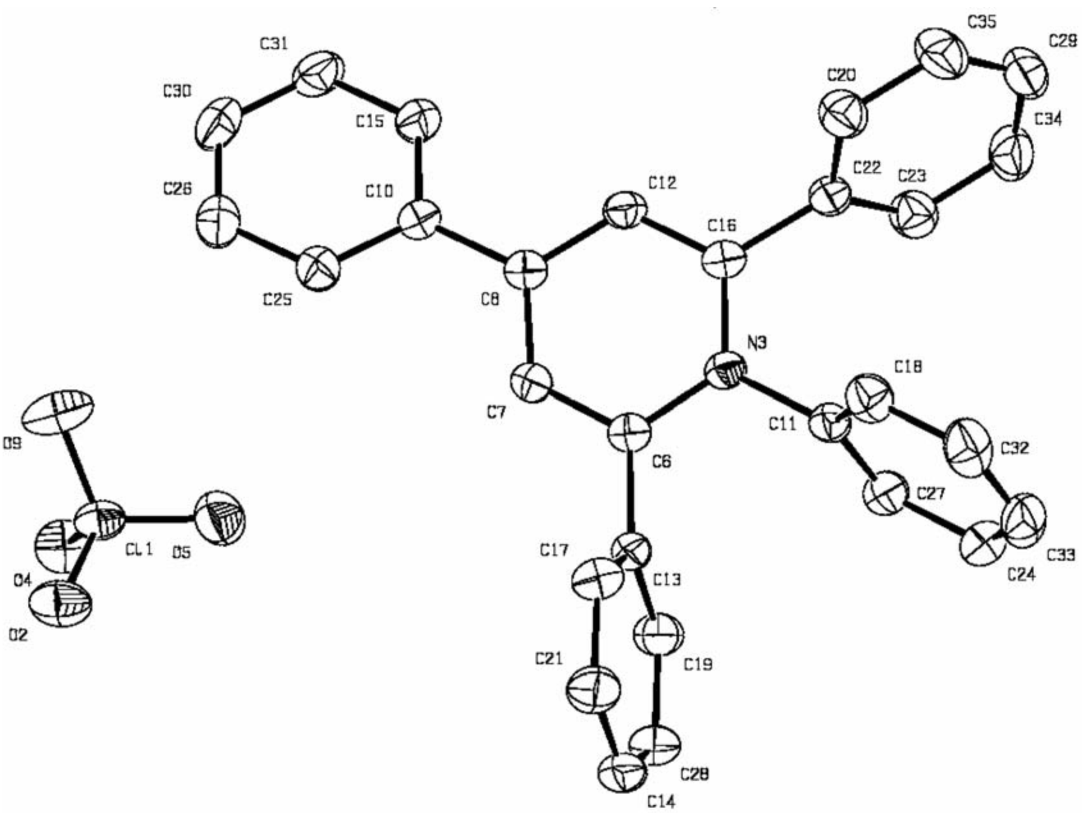

Fig. 2. Molecular structure and atom numbering of 1,2,4,6-tetraphenylpyridinium perchlorate.

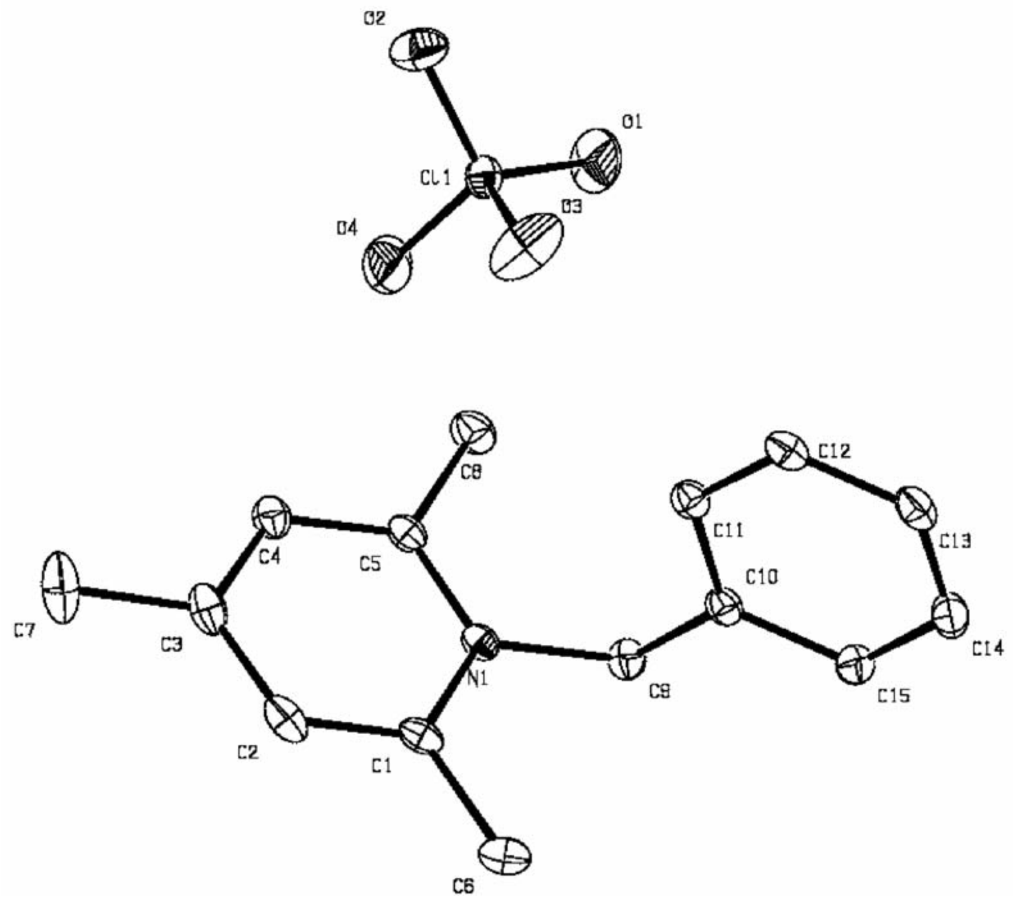

Fig. 3. Molecular structure and atom numbering of 1-benzyl-2,4,6-trimethylpyridinium perchlorate.

Results and discussion

In this work, structural data of two perchlorates that have already been described in literature, 1,2,4,6-tetraphenylpyridinium perchlorate and 1-benzyl-2,4,6-trimethylpyridinium perchlorate are published for the first time. Basic crystallographic data are given in Table 3.

Both structures (Figs. 2 and 3) are formed by the relevant cation and a perchlorate anion. Oxygen atoms of perchlorates are usually disordered in such structures. Disorder of perchlorates in the structure depicted in Fig. 2 (1,2,4,6-tetraphenylpyridinium perchlorate) was not solved using an exactly calculated model. The structure in Fig. 2 is depicted as "average structure" which causes somewhat "ugly" thermal ellipsoids especially on oxygen atoms.

The following model was used to describe the disorder of the perchlorate anion in the second structure depicted in Fig. 3 (1-benzyl-2,4,6-trimethylpyridinium perchlorate): O1 atom is fixed in one position and it is not disordered, while atoms O2, O3, and O4 were found in two positions (O2A, O3A, and O4A). The same occupation factors were refined for all three remaining oxygen atoms and fixed on the value of 0.56/0.44. Oxygen atoms O2A, O3A, and O4A are not depicted in Fig. 3 for clarity and they are "hidden" in thermal ellipsoids.

However, both cations contain quaternary nitrogen and thus cannot participate in the network of short hydrogen bonds. In addition, they crystallise quite readily. However, to induce proton conductivity in the prepared substances, the perchlorate cation has to be replaced by a hydrogen anion, which was not achieved in spite of multiple attempts.

Thus, the pyridinium salt preparation employing cations with the general formula given in the introduction which correspond to the commercially available amines 4-methylpyridine, 5-ethyl-2-methylpyridine, and 2,4,6-trimethylpyridine was attempted. Methylation of the first two amines on the nitrogen atom yielded the corresponding iodides, while benzylation yielded the corresponding bromides. *N*-substituted halogenides derived from 2,4,6-trimethylpyridine could not be isolated in sufficient amounts. Halogenides prepared in this way were converted to aqueous solutions of the corresponding hydroxides using silver oxide. Successful progress of the conversion was monitored by mass spectroscopy. Concentrations of the hydroxide solutions were determined by titration with a standard solution of sulphuric acid; these solutions were then used to prepare the acidic salts. How-

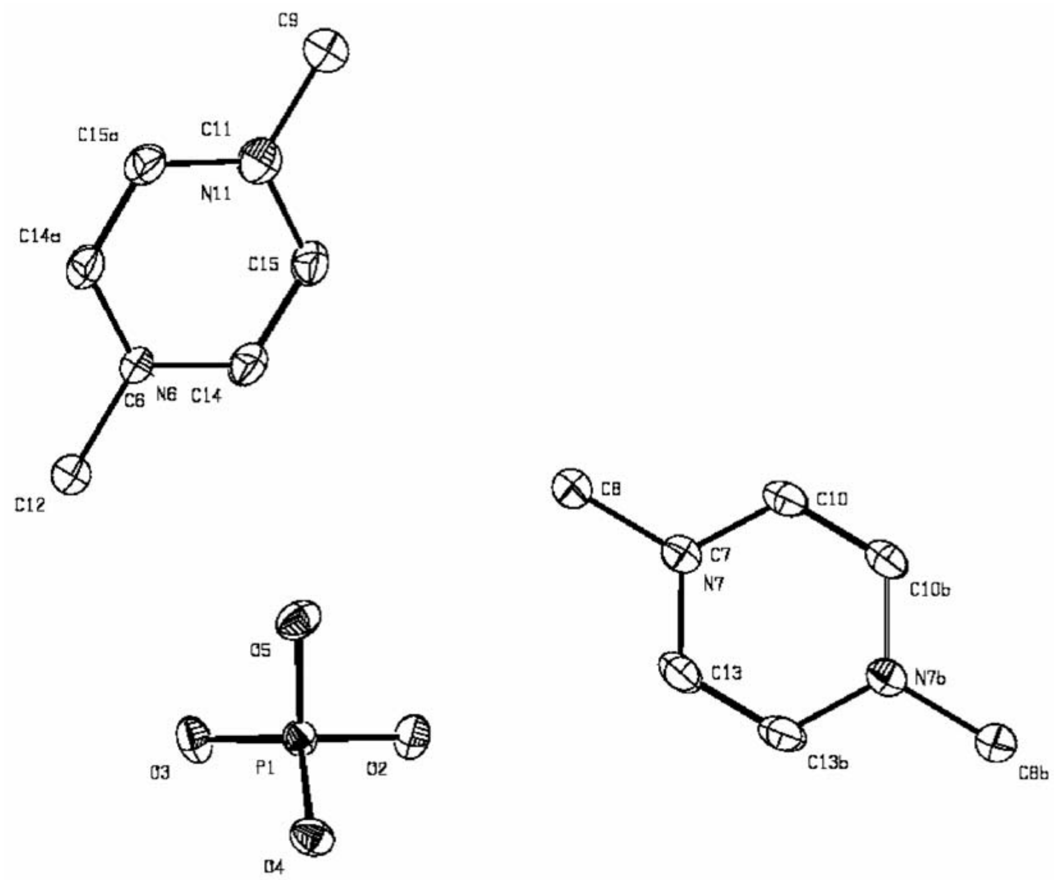

Fig. 4. Molecular structure and atom numbering of 1,4-dimethylpyridinium dihydrogen phosphate (*IV*).

ever, for the *N*-benzyl derivatives, the concentrations of the hydroxide solutions obtained were too low (the reaction with Ag_2O progressed with a very low yield) and thus the attention was further concentrated on the *N*-methyl derivatives. Based on experience from previous works, preparation of the corresponding hydrogen sulphates, dihydrogen phosphates, hydrogen selenates, and hydrogen selenites through a reaction with the corresponding mineral acids was attempted. However, the reactions with selenic acid did not lead to any crystalline products, while selenious acid oxidised the methyl group in the para position of the pyridinium ring to a carboxyl group and thus, only hydrogen sulphates and dihydrogen phosphates were considered in the following work.

The described procedure enabled the isolation of four salts: 1,4-dimethylpyridinium hydrogen sulphate, 1,4-dimethylpyridinium dihydrogen phosphate, 1,2-dimethyl-5-ethylpyridinium hydrogen sulphate, and 1,2-dimethyl-5-ethylpyridinium dihydrogen phosphate. All the synthesised substances (see the Experimental section) form highly hygroscopic crystalline materials very difficult to free of water. Elemental analysis indicates lower carbon and nitrogen contents while their corresponding molar ratios is maintained, which results from the presence of water. The NMR and FTIR spectra correspond to the formulation of the prepared salts. However, only in one case, 1,4-dimethylpyridinium dihydrogenphosphate, the removal of a single crystal suitable for X-ray structural analysis from the crystalline material was achieved. Basic crystallographic data for this substance are given in Table 3, and the independent part of the structure is presented in Fig. 4.

The structure of this substance contains three basic motifs: one dihydrogen phosphate and two 1,4-dimethylpyridinium cations, although the stoichiometry of the salt is 1 : 1. Each of the cations contributes only by one half to the independent part, while the second half is generated by symmetry operation. For cations with carbon C7 and nitrogen N7, occupation of 0.5 was found for the studied structural data on these atoms, while occupation of 1 was found for the other atoms. Occupations of 0.5 on carbon C7 and nitrogen N7 is caused by disorder as carbon and nitrogen alternate in their positions with a fifty percent probability. For the second unit, occupation of 0.25 was found on atoms C11 and N6 due to the similar alternation of carbon and nitrogen and, in this case, also due to the special position of atoms C11 and N6. Dihydrogen phosphate anions in Fig. 5 are connected by hydrogen bonds with the length of 2.5666(3) Å (O5—H1$\cdots$O4) and 2.5572(3) Å (O2—H2$\cdots$O3), and angles (O—H$\cdots$O) of 175° and 178°, respec-

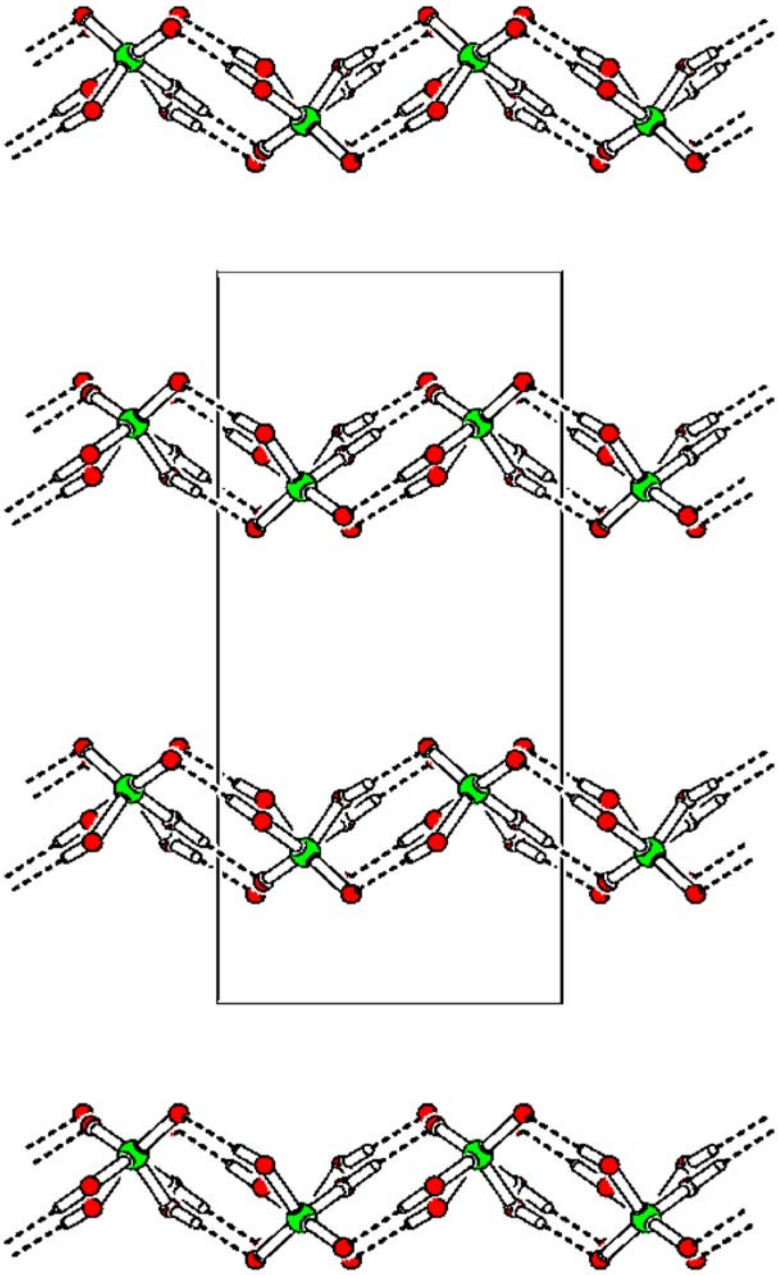

Fig. 5. Dihydrogenphosphate chains in the structure of 1,4-dimethylpyridinium dihydrogen phosphate. Organic part omitted for clarity.

tively. These anion chains in the direction of crystallographic axis *c* are not mutually connected by other hydrogen bonds and can thus be considered to be “one-dimensional”. This structure contains therefore motifs that determine the ability of the substance to carry protons, like in the case of amino guanidinium(1+) dihydrogen phosphate (Němec et al., 2004), 1,4-diazabicyclo[2.2.2]octane-1,4-diium dihydrogen phosphate monohydrate (Smrčok et al., 2009; Kaman & Havlíček 2005), and other similar compounds (Taraba, 2012). Consequently, the anion network is connected by sufficiently short hydrogen bonds that pass through the structure in a single, given direction. Proton conductivity can thus be anticipated. However, in order to verify this expectation, it is necessary to grow a sufficiently large single crystal of this substance and to measure its anisotropic properties.

Conclusions

Several salts of phosphoric, sulphuric, and perchloric acid with 1,4-dimethylpyridinium, 1,2-dimethyl-5-ethylpyridinium, 1,2,4,6-tetraphenylpyridinium, and

1-benzyl-2,4,6-trimethylpyridinium were prepared and studied. Crystal structures of 1,2,4,6-tetraphenylpyridinium perchlorate, 1-benzyl-2,4,6-trimethylpyridinium, and 1,4-dimethylpyridinium dihydrogen phosphate were solved. In the last mentioned structure, the network of dihydrogenphosphate anions contains short hydrogen bonds (approximately 2.55 Å) which form infinite chains throughout the structure (see Fig. 5). This structure motif can lead to long-distance transfer of protons through the crystal and the compound can act as a proton conductor.

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