Structural and Electrical Conductivity Properties of a Newly Synthesized 3-Methoxybenzylammonium Cation Diphosphate

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Abstract: The structure of the newly synthesized material, [3-(CH₃O)C₆H₄CH₂NH₃]₂H₂P₂O₇ can be described as inorganic layers (H₂P₂O₇²⁻)_n stacked perpendicular to the c-axis at $z = 0$ and $z = \frac{1}{2}$ interleaved with organic cations [3-(CH₃O)C₆H₄CH₂NH₃]⁺. The connection of the independent entities are assured by a set of N—H...O and C—H...O H-bonds in addition to electrostatic and Van der Waals interactions, generating a non-centrosymmetric three-dimensional network. On the basis of electrical conductivity measurements, it was found that, at higher temperature conductivity increases linearly, showing medium conducting behaviour of the organic diphosphate salt with values lying in the range of $\sigma = 0.69 \cdot 10^{-4} \Omega^{-1}\text{cm}^{-1}$ at 328 K to $2.66 \cdot 10^{-4} \Omega^{-1}\text{cm}^{-1}$ at 405 K and activation energy of $E_a = 0.23 \text{ eV}$. Its characterization by IR absorption spectroscopy is described too.

Keywords: Chemical synthesis, X-ray crystal structure, Electrical conductivity, Infrared spectroscopy.

Introduction

Organic and inorganic phosphates have several applications in different areas because of their use as solid electrolytes, catalysis and non-linear optic materials¹⁻³. For optical applications in telecommunication, optical data storage and information processing make particularly the non-centrosymmetric materials of strategic importance especially when endowed with electrical conduction properties⁴.

Many approaches for forming acentric structures have been followed and hydrogen bonded networks appear to be the most exciting among all these approaches since they have been recognized as the steering force responsible for the formation of acentric structures³. The approach of this new engineering has been applied to many organic cations encapsulated in host anionic matrices. Among the about twenty seven related structures of organic cation diphosphates, only two non-centrosymmetric structures are reported⁵⁻⁶. The crystal structure of the title compound provides a new example of non-centrosymmetric arrangement; [3-

$(\text{CH}_3\text{O})\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3]_2\text{H}_2\text{P}_2\text{O}_7$. Its synthesis, crystal structure and characterization are described.

Experimental

Synthesis of $[3-(\text{CH}_3\text{O})\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3]_2\text{H}_2\text{P}_2\text{O}_7$

The chemical synthesis of the title compound was performed in two steps. In the first step, a concentrated aqueous solution (20 ml) of diphosphoric acid (210-2 mol) was prepared from $\text{Na}_4\text{P}_2\text{O}_7$ by using an ion exchange resin (Amberlite IR 120). In the second step, this solution was immediately neutralized with an alcoholic solution (5ml) of 3-méthoxybenzylamine (410-2 mol) with constant and rapid stirring according to the following reactional scheme:

In a few days colorless prismatic crystals appear after evaporation of the solution at room temperature. The so obtained materials are washed several times with hot water and dried in air.

Crystal structure determination

Experimental conditions and crystal data used during the measurement of diffracted intensities are given in Table 1. The intensity data were collected at room temperature using an Enraf-Nonius Mach3 diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.7107\text{\AA}$). The cell parameters were determined from a least square refinement of 25 reflections. Two standard reflections were periodically measured for every 120 min during data collection. Unique reflections 4509 were measured of which only 3295 had $I > 2\sigma(I)$ and were used for structure determination and refinement. The structure was solved by direct method using the program SHELXS-977 in the WinGX package⁸ and refined by full-matrix least-squares method with the program SHELXL-977. All non-hydrogen atoms were refined isotropically and then anisotropically by full-matrix least-squares method. All hydrogen atoms were placed geometrically and treated as riding. An ORTEP9 drawing of the molecular structure is shown in Fig. 1. The main geometrical features of the hydrogen-bond scheme are provided in Table 2.

Figure1. ORTEP View of the asymmetric unit of $[3-(\text{CH}_3\text{O})\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3]_2\text{H}_2\text{P}_2\text{O}_7$ with atom labels and 30% probability displacement ellipsoids for non- H atoms.

Supplementary material

Crystallographic data (CIF) for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data centre as supplementary materials No CCDC 764780.

Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB12EZ, UK (Fax: +44(1223) 336-033; email: deposit@ccdc.cam.ac.uk).

Electrical measurements

IR spectrum of $[3-(\text{CH}_3\text{O})\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3]_2\text{H}_2\text{P}_2\text{O}_7$ was recorded at room temperature with a Perkin Spectrum BXII spectrometer over the wave number range of $4000\text{--}400\text{ cm}^{-1}$ with a resolution of about 2 cm^{-1} . A thin transparent pellet was made by compacting an intimate mixture obtained by shaking 2 mg of the samples in 100 mg of KBr.

Conductivity measurements were carried out on a pressed powder in the frequency range of 10 Hz to 13 MHz, with an applied voltage of 10 mV. Sample pellets, 11 mm in diameter and 1.5–2.0 mm in thickness, were made by pressing 200–400 mg of the hybrid material under a pressure of 12-tons, at room temperature. Metallic silver was deposited on both sides, which served as electrodes. The pellet was placed between two blocking electrodes in a tubular furnace, submitted to a temperature regulator. The electrical conductivity measurements were carried out from room temperature to 405 K, with 5–15 K steps, by checking the complex impedance spectroscopy with a Hewlett-Packard 4129A impedance analyzer.

Table 1. Crystal and experimental data of $[3-\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{NH}_3]_2\text{H}_2\text{P}_2\text{O}_7$.

Empirical formula	$\text{C}_{16}\text{H}_{26}\text{N}_2\text{P}_2\text{O}_9$
Formula weight (g.mol^{-1})	452.3
T(K)	293
Wavelength ($\text{\AA}$)	0.7107
Crystal system	Orthorhombic
Space group	$\text{P2}_1\text{2}_1\text{2}_1$
a ($\text{\AA}$)	9.123 (3)
b ($\text{\AA}$)	14.065 (5)
c ($\text{\AA}$)	31.897 (4)
V ($\text{\AA}^3$)	4093 (2)
Z	8
$D_{\text{calc}}, \text{g.cm}^{-3}$	1.468
$\mu(\text{MoK}\alpha), \text{mm}^{-1}$	0.26
F(000)	1904
Reflections collected, R_{int}	4509, (0.03)
Observed data ($I > 2(\sigma)$)	3295
No. of variables	516
Goodness-of-fit	1.05
R	0.077
Rw	0.228

Results and Discussion

Structure description

The asymmetric unit of the title compound (Fig.1) consists of two anions $[\text{H}_2\text{P}_2\text{O}_7]^{2-}$ and four organic cations $[\text{3}-(\text{CH}_3\text{O})\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3]^+$ crystallographically independent. As shown in Fig. 2, the atomic arrangement of 3-methoxybenzylammonium dihydrogenodiphosphate is non-centrosymmetrical. The four independent cations $[\text{3}-(\text{CH}_3\text{O})\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3]^+$, occupy the interlayer spaces and establish with the anionic framework N—H...O hydrogen bonds.

The $[\text{H}_2\text{P}_2\text{O}_7]^{2-}$ anions are connected by hydrogen bonds to form inorganic layers parallel the *ab* plane around $z = 0$ and $z = 1/4$. The established hydrogen bonds are of different types. The O—H...O involving four short contacts ranging from 2.547 Å to 2,574 Å (Table 2), ensure the connection between $[\text{H}_2\text{P}_2\text{O}_7]^{2-}$ groups in the same inorganic layer. The other types of interactions N—H...O and C—H...O originating from the organic ions assuring the connection between the organic molecules and the anion layers. These hydrogen bonds, participate with the additional interactions (electrostatic, Van der Waals, π ... π , etc..) to the cohesion and the stability of the crystal structure.

In this structure, the PO₄ tetrahedra are linked by two bridging oxygen atoms O(4) and O(11) to give the H₂P₂O₇ groups. In PO₄ tetrahedron, the P—O distances vary from 1.475(6) Å to 1.607(6) Å. The values of O—P—O angles vary from 101.6(4) to 118.2(4)°, whereas those of POP angle bridge groups are P(1)—O(4)—P(2)= 134.3(4)° and P(3)—O(11)—P(4)= 134.6(4)°. These values are in conformity with the results found for other diphosphates¹⁰⁻¹². Regarding the cations arrangement, the protonated 3-methoxybenzylamine molecules are hydrogen bounded to anionic sub-network by rather long N—H...O and C—H...O bonds with distances ranging N...O = 2.746 – 3.156 Å and C ...O = 3.481 – 3.556 Å. The C—H...O bonds are already been evidenced by several authors in molecular crystals¹³⁻¹⁵. The density of this H-bond scheme constitutes probably the main factor responsible for the formation of a non-centrosymmetric material³.

Figure 2. Projection along the *a* direction of the atomic arrangement in $[\text{3}-(\text{CH}_3\text{O})\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3]_2\text{H}_2\text{P}_2\text{O}_7$.

Figure 3. Topology of H-bond scheme in $[3-(\text{CH}_3\text{O})\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3]_2\text{H}_2\text{P}_2\text{O}_7$.

IR spectroscopic investigation

The IR spectrum of the title compound is given in Fig. 4. We have assigned the IR bands to vibration modes based on spectroscopic studies on diphosphates 17-22. The broad bands which appear between 3400 and 2800 cm^{-1} are assigned to stretching vibrations of organic and hydroxyl groups $\nu(\text{C-H})$, $\nu(\text{N-H})$ and $\nu(\text{O-H})$ and $\nu(\text{C}_{\text{aryl}}\text{-H})$ 21. Those located between 1660–1200 cm^{-1} correspond to bending and stretching modes $\delta(\text{N-H})$, $\nu(\text{C-C})$ and $\nu(\text{C-N})$ 22. The bands of bending vibrations of $\delta(\text{C-N})$ and $\delta(\text{C-O-C})$ are located between 1340–1041 cm^{-1} but those observed between 970 and 630 cm^{-1} correspond to bending vibrations of $\delta(\text{C}_{\text{aryl}}\text{-H})$ characteristic of di-substituted benzene 21-22.

Table 2. Main interatomic distances ($\text{\AA}$) and angles ($^\circ$) involved in the hydrogen bond scheme of $[3\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{NH}_3]_2\text{H}_2\text{P}_2\text{O}_7$.

D-H...A	D-H	H...A	D...A	D-H...A
O3-HO3...O6	0.820	1.815	2.574	153.34
O8-HO8...O2	0.820	1.767	2.563	163.31
O5-HO5...O13	0.820	1.938	2.560	131.98
O12-HO12...O9	0.820	1.780	2.547	155.14
N1-H1A...O7	0.890	2.076	2.773	134.52
N1-H1B...O14	0.890	1.940	2.794	160.43
N1-H1C...O6	0.890	1.921	2.780	161.75
N2-H2A...O13	0.890	1.994	2.843	159.26
N2-H2B...O10	0.890	2.016	2.905	176.81
N2-H2B...O9	0.890	2.623	3.156	119.37
N2-H2C...O1	0.890	1.962	2.832	165.43
N3-H3A...O1	0.890	2.041	2.804	143.10
N3-H3B...O10	0.890	1.930	2.746	151.60
N3-H3C...O9	0.890	1.968	2.806	156.24
N4-H4A...O7	0.890	2.008	2.896	176.04
N4-H4B...O2	0.890	2.027	2.887	162.07
N4-H4C...O14	0.890	1.962	2.810	158.76
C3- H3...O13	0.930	2.580	3.508	176.00
C17- H17A...O8	0.970	2.590	3.556	171.00
C19- H19...O2	0.930	2.560	3.481	173.00

The symmetric and asymmetric stretching vibrations (vs,vas) of the PO₃ terminal group are observed between 1260 and 975 cm⁻¹, but those ranging from 610 to 340 cm⁻¹ are attributed to bending vibrations (δs,δas) of the same group. The bands observed between 960 and 675 cm⁻¹ correspond to the stretching symmetric and asymmetric modes of POP bridge group¹⁷⁻²².

Electrical Conductivity Analysis

Electrical conductivity measurements were done on [3-(CH₃O)C₆H₄CH₂NH₃]₂H₂P₂O₇. Some complex impedance diagrams (-Im. Z (Ω) versus Real Z (Ω)) recorded at different temperatures are given in Fig. 5. The conductivity σ of the studied compound was calculated using the following equation $\sigma = d/AR$, where d, A, and R represent the thickness, the area, and the resistance, respectively. The resistance was obtained from the intercept of the Nyquist plot with the real axis. The temperature dependence of the conductivity between 328 K and 405 K is represented in Fig. 6 in the form of Ln (σT) versus 103/T. In this range of temperature, the electrical conductivity increases with rising temperature and the conductivity has approximately an Arrhenius type behaviour $\sigma = A/T \exp(-E_a/KT)$, where A is a constant depending on the material, K the Boltzmann constant and E_a the activation energy determined by the slope of the interpolating Arrhenius curve ($E_a = 0.23$ eV). No break in the curve is observed, this seems to indicate only one protonic conductivity mechanism and there is no modification of the electrical properties. These results are in good agreement with the thermal study which shows no phase transition in this temperature range that can influence the conduction mechanism.

Figure 4. IR absorption spectrum of [3-(CH₃O)C₆H₄CH₂NH₃]₂H₂P₂O₇.

On the basis of the literature²³⁻²⁷, the electric properties of this hybrid compound may be interpreted by the following way: The increase of temperature can favour the vibration of H₂P₂O₇²⁻ anionic chains, which induce a rapid reorientation of H₂P₂O₇²⁻ and a fast moving of the H⁺ protons²³. The range of ionic conductivity that goes from $\sigma = 0.69 \cdot 10^{-4} \Omega^{-1}\text{cm}^{-1}$ at 328 K to $2.66 \cdot 10^{-4} \Omega^{-1}\text{cm}^{-1}$ at 405 K and the value of the activation energy, are of the same order of magnitude with that given by other organic cation phosphates²³⁻²⁷.

Figure 5. Typical impedance spectra of $[3-(\text{CH}_3\text{O})\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3]_2\text{H}_2\text{P}_2\text{O}_7$ at various temperatures.

Figure 6: Arrhenius plot of the electrical conductivity of $[3-(\text{CH}_3\text{O})\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3]_2\text{H}_2\text{P}_2\text{O}_7$.

Conclusion

In the non-centrosymmetric title compound, $[3-(\text{CH}_3\text{O})\text{C}_6\text{H}_4\text{CH}_2\text{NH}_3]_2\text{H}_2\text{P}_2\text{O}_7$, the diphosphate anions and the organic cations are linked together by a set of N—H...O and C—H...O H-bonds in addition to electrostatic and van der Waals interactions, generating a three-dimensional network. The electrical conductivity and the activation energy properties of this material are of the same of magnitude with that given by other semi-conductor phosphates, which may be due to the incorporation of ionic entities which increase the ionization tendency.

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