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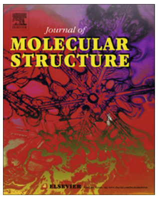

Growth and characterization of *L*-prolinium phosphite

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HIGHLIGHTS

- New *L*-prolinium phosphite crystal was grown.
- Crystal structure was determined.
- The crystal is characterized by vibrational spectral, thermal, NLO properties.

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ABSTRACT

Single crystal of *L*-prolinium phosphite was grown by evaporation method from aqueous solution. It crystallizes in the orthorhombic system (space group $P2_12_12_1$, $Z = 4$). The asymmetric unit contains one *L*-prolinium cation and one phosphite $(HPO_2(OH))^-$ anion. The phosphite anions form a chain by hydrogen bond O—H…O with O…O distance 2.5601(15) Å parallel [010]. The *L*-prolinium cations bridge two chains of anions by O—H…O and N—H…O hydrogen bonds with O…O and N…O distances 2.505(2) Å and 2.718(2) Å respectively. The infrared and Raman spectra are registered and discussed. Thermal behavior was studied. Phase-matched SHG was observed.

Introduction

Salts of amino acids attracted researchers' attention from different points of view, particularly, as possible nonlinear optical (NLO) materials [1]. Salts of *L*-proline were considered as possible NLO materials along with salts of other amino acids. *L*-Prolinium hydrogen tartrate [2], *L*-prolinium trichloroacetate [3] and two forms of *L*-prolinium picrate (orthorhombic [4] and monoclinic [5]) were obtained and later investigated as possible NLO materials. Also crystal of di-*L*-prolinium hexafluorosilicate ($(L\text{-ProH})_2SiF_6$) was obtained [6]. In addition to these simple salts, salts with dimeric cation (*L*-proline… *L*-prolinium) nitrate [7] and (*L*-proline… *L*-prolinium) perchlorate [8] were obtained and investigated. Later other similar new salts were obtained in our group: (*L*-proline… *L*-prolinium) chloride, (*L*-proline… *L*-prolinium) bromide and (*L*-proline… *L*-prolinium) tetrafluoroborate [9]. In continuation of this work we investigated the possibility of formation of such salt with phosphite $(HPO_2(OH))^-$ anion. However, we found that in the system *L*-proline + H_3PO_3 + H_2O only a simple salt with 1:1 ratio, namely, *L*-prolinium phosphite is formed [1]. Previously phosphites of four achiral amino acids, namely, glycine [10], sarcosine [11], betaine [12] and β-alanine [13] and also two chiral amino acids, namely, *L*-histidine [14] and *L*-tryptophan [15] were obtained and investigated. In addition to these simple salts only one crystal with dimeric cation is known with phosphite anion, namely, *L*-alanine… *L*-alaninium phosphite monohydrate [16]. There is one more report on *L*-valinium phosphite [17], which as was shown in [1], actually is *DL*-valinium phosphite.

The aim of the present work is to report our results on crystal growth, crystal structure determination, vibrational spectroscopic, thermal and second harmonic generation characterization of the $(L\text{-ProH})H_2PO_3$ crystal.

Experimental

Synthesis

As initial reagents we used *L*-proline and phosphorous acid purchased from Sigma Chem. Co. The salt of $(L\text{-ProH})H_2PO_3$ was obtained from aqueous solution containing equimolar quantities

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of *L*-proline and phosphorous acid (H_3PO_3) by slow evaporation at room temperature. The crystal (*L*-ProH)H_2PO_3 was obtained in our group in course of searching new salts of amino acids with dimeric (A…A^+) type cations. From aqueous solution at 2:1 M ratio of *L*-Pro and H_3PO_3 anhydrous *L*-proline is formed. At molar ratios 1.5:1 and 1:1 of *L*-proline and H_3PO_3 identical crystals were formed. The IR spectrum indicated the presence of short hydrogen bonds and we did not rule out the formation of a salt with a dimeric cation, however, the structure determination showed that its composition is 1:1.

Crystal structure determination

Suitable crystals of (*L*-ProH)H_2PO_3 were manually selected and checked for irregularities under the microscope. A well-developed crystal with the approximate size of 0.12 × 0.10 × 0.08 mm^3 was and mounted on a glass needle with laboratory grease. Single-crystal X-ray intensity data of (*L*-ProH)H_2PO_3 were obtained by a measurement on a Bruker APEX II diffractometer, equipped with a graphite monochromator and using Mo Kα (λ = 0.71073 Å) radiation. The structure was solved using direct methods; subsequent difference Fourier syntheses and least-square refinements yielded the positions of the remaining atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters, hydrogen atoms with isotropic displacement parameters. The hydrogen atoms were treated as riding on their parent atoms, except for the hydrogen atom of the acid group of the *L*-prolinium cation and those of the hydrogen phosphite anion. All calculations were performed using the Bruker instrument software and the SHELX97 program package [18–20].

The crystallographic data as well as details of the measurement are listed in Table 1. Further crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033), citing the title of this paper and the CCDC No. 955460.

Vibrational spectra

Attenuated total reflection Fourier-transform infrared spectra (FTIR ATR) were registered by a Nicolet 5700 spectrometer (ZnSe prizm, Happ-Genzel apodization, ATR distortion is corrected, number of scans 32, resolution 4 cm^{-1}). Part of the IR spectrum in the region 500–400 cm^{-1} was taken from FTIR spectra registered with Nujol mull (4000–400 cm^{-1}, number of scans 32, resolution 2 cm^{-1}).

Table 1
Crystal data and details of the refinement for *L*-prolinium phosphite.

Formula	$C_5H_{12}NO_5P$
M_r	197.13
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	6.1161(3)
b (Å)	9.4681(4)
c (Å)	15.5867(7)
V (Å^3), *Z*	902.59(7), 4
D_{calc} (g cm^{-3})	1.451
μ (Mo Kα) (cm^{-1})	0.291
F (000)	416
T (K)	296(2)
hkl range	−6/9, −15/12, −25/17
Reflections measured	12318
Reflections unique	3852
Data with ($F_o > 4\sigma$ (F_o))	3157
R_{int}	0.0388
Parameters refined	130
Flack parameter [21]	−0.02(9)
$R(F)^*$(for $F_o > 4\sigma$ (F_o))	0.0420
$wR(F^2)^*$ (all reflections)	0.1132
Weighting parameters *a*, *b*	0.0613/0.0925
$\Delta\rho_{fin}$ (max/min) [e Å^{-3}]	0.463/−0.305

* $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = [\Sigma\, w(F_o^2-F_c^2)^2/\Sigma\, wF_o^4]^{1/2}$, $w = 1/[\sigma^2(F_o^2)+(a\times P)^2 + b\times P]$, $P = (F_o^2+2F_c^2)/3$.

Fourier-transform Raman spectra were registered by a NXR FT-Raman Module of a Nicolet 5700 spectrometer: number of scans: 2048, laser power at the sample: 0.41 W, resolution 4 cm^{-1} at room temperature.

Thermal properties

For the study of thermal properties we employed a Paulik–Paulik–Erdey Derivatograph (MOM, Hungary) (temperature range: 20–500 °C, the mass of specimen: 100 mg, heating rate: 5 °C/min in air atmosphere) and also a Boëtius type microscope with heating stage (in the range 20–350 °C).

Results and discussion

Crystal growth

Single crystal of (*L*-ProH)H_2PO_3 with 14 × 11 × 5 mm^3 dimensions was grown from aqueous solution containing equimolar quantities of components by slow evaporation method at 28 °C during 6 days. In Fig. 1 the grown crystal with calculated morphology obtained using Mercury 3.3 program is shown. The top face was the bottom during crystal growth.

Molecular and crystal structure of L-prolinium phosphite

As proline is a cyclic amino acid with the nitrogen atom within the five-membered ring, we considered the possibility of disorder within the ring, i.e. the possible disorder of nitrogen and carbon (as it is found e.g. for *L*-prolinium hydrogen *L*-tartrate [2] and monoclinic form of *L*-prolinium picrate [5] as well as in (*L*-proline… *L*-prolinium) perchlorate [8]). However, the refinement gave the best agreement for an ordered model, which is supported by the hydrogen bond extending from the nitrogen atom.

The asymmetric unit contains one formula unit (*L*-ProH)H_2PO_3 (Fig. 2). Selected bond lengths as well as valence and torsion angles are collected in Table 2. Geometric parameters of phosphite anions have expected values (compare e.g. with respective values in the structure of *L*-histidinium phosphite [14]). The same is true for *L*-prolinium cation. Bond lengths in pyrrolidine ring also have typical values. Conformation of pyrrolidine ring is determined by the following torsion angles: $\chi^1(-38.2(2)°)$, $\chi^2(37.8(3)°)$, $\chi^3(-22.9(3)°)$, $\chi^4(-1.5(2)°)$, $\theta(24.71(18)°)$ (see Table 2). The bond lengths in carboxyl group (C═O(1.2058(18) Å) and C—OH(1.294(2) Å) are in the range of expected values. The $H_2PO_3^-$ anions form infinite chains by O3—H3…O4(2.5601(15) Å) hydrogen bonds (Fig. 3). Another stronger hydrogen bond toward the anion extends from the carboxyl group of the prolinium cation, namely O1—H1…O5(2.505(2) Å). The hydrogen atom H12 of the NH_2^+ group forms a relatively short hydrogen bond N1—H12…O4(2.718(2) Å) towards the anion, while the atom H11 has three contacts: one is intramolecular with carbonyl oxygen atom O2 with distance H11…O2(2.31 Å), the second also with O2 atom, but intermolecular with nearest cation with distance H11…O2(2.24 Å) and the third contact with O5 atom of anion H11…O5(2.36 Å). All these three contacts are in the 2.15–2.45 Å intermediate interval between weak hydrogen bonds and strong van der Waals bonds.

When investigating the packing of the units within the crystal, the infinite chains along [0 1 0] formed by the anions alternate with layers of *L*-prolinium cations (Fig. 4).