



The study of crystal structures and vibrational spectra of inorganic salts of 2,4-diaminopyrimidine



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ABSTRACT

Six novel salts of 2,4-diaminopyrimidine were prepared and studied by X-ray single-crystal structure analysis and vibrational spectroscopy. All but one of the title compounds, *i.e.* (2,4-diaminopyrimidine) 2,4-diaminopyrimidinium perchlorate, 2,4-diaminopyrimidinium nitrate, 2,4-diaminopyrimidinium perchlorate, bis(2,4-diaminopyrimidinium) hydrogen phosphate tetrahydrate and bis(2,4-diaminopyrimidinium) selenate dihydrate, crystallize in the triclinic system with the centrosymmetric space group $P\bar{1}$ while the crystals of the remaining compound – 2,4-diaminopyrimidinium chloride hemihydrate – belong to the monoclinic system (space group $C2/c$). All the crystal structures contain the characteristic graph set motif $R_2^2(8)$ with N–H...N hydrogen bonds. This graph set motif can be formed by one of three possible arrangements of a pair of 2,4-diaminopyrimidinium cations and all these arrangements have been observed in the title structures. The title salts were also investigated by vibrational spectroscopy (FTIR and FT Raman). The presented interpretation of the vibrational spectra is based on DFT calculations of 2,4-diaminopyrimidine molecule and 2,4-diaminopyrimidinium cation.

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1. Introduction

The crystal engineering is a general branch of supramolecular chemistry, which covers processes of purposeful design of functional three-dimensional crystal structures from molecule-scale components. It actually represents one of the most promising fields of the design of novel materials with desired properties. However, the synthesis of crystals is a much more difficult process to control since it involves manipulation of simultaneous effects of long- and short-range interactions while kinetic effects are difficult to take into account. Hydrogen bonds and dipolar interactions may play most important role in interconnection of synthons.

Formation of a crystal from molecules and ions depends not only on symmetry and size of the molecules involved but mainly on intermolecular (supramolecular) interactions, which control mutual assembly of building blocks. From the whole range of these interactions of a different nature (*i.e.* particularly ion–ion interactions, ion–dipole interactions, dipole–dipole interactions, cation– π interactions, anion– π interactions, π – π interactions and the van der Waals forces) the hydrogen bonds can be considered as

the most important and powerful ones, which are sometimes classified as dipole–dipole interactions. Hydrogen bonds can also act as effective means how to override tendency of organic bases with high dipole moments to form centrosymmetric pairs.

2,4-diaminopyrimidine and its derivatives are successfully used in the field of medical research. They can act as antagonists of allergic rhinitis or solid tumours [1,2], inhibitors of cancer cells [3], antifilarial agents [4] and DNA modifiers [5–7]. But only one crystal structure containing 2,4-diaminopyrimidinium cation with inorganic acid is present in the Cambridge Structural Database [8]. This is the crystal structure of bis(2,4-diaminopyrimidinium) sulphate monohydrate [9] (REFCODE TEGZIO).

This work is a part of our project which is focused on preparation and study of new materials with potential non-linear optical (NLO) properties. We are mainly interested in compounds which are composed of heteroaromatic nitrogen-containing organic bases and inorganic oxyacids and where variety of hydrogen bonds is expected. The formation of crystalline salts with different anionic species (ranging from simple chlorides to planar nitrates or tetrahedral sulfates, selenates, perchlorates or phosphates), which also differ in their role as proton donors/acceptors, can lead to non-centrosymmetric phases which are suitable for nonlinear optics [10–21]. Unfortunately, all the title structures are centrosymmetric

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and therefore our attention has been focused mainly on crystallographic and spectroscopic point of aspects.

The other motivation for this paper has been the fact that the description of different arrangements of the title cation in the solid state has been neglected. This cation is also interesting for investigation of the configuration of the primary-amine group [22]. The Cambridge Structural Database yielded only five crystal structures containing diaminopyrimidinium cations with the following REFCODES: DICCOJ – 2,3-diaminopyrimidinium 4-nitrophenol 4-nitrophenolate [23]; TEGZIO – bis(2,4-diaminopyrimidinium) sulphate monohydrate [9]; TEGZIO01 – hydroxonium bis(2,4-diaminopyrimidinium) phosphate [24]; WUJROI – 2,6-diaminopyrimidinium 1,3-cyclopentanedionate monohydrate [25] and WUJRUO – 2,6-diaminopyrimidinium 1,3-cyclohexanedionate 1,3-cyclohexanedione enol monohydrate [25]. Very questionable crystal structure of TEGZIO01 surprisingly exhibits the same lattice parameters and the positional parameters of the non-hydrogen atoms as TEGZIO. Therefore TEGZIO01 has been excluded from other considerations and discussion.

The present study is focused on crystal structures and vibrational spectra of six new compounds: 2,4-diaminopyrimidinium chloride hemihydrate (**dapClH₂O**), (2,4-diaminopyrimidine) 2,4-diaminopyrimidinium perchlorate (**dap₂ClO₄**), 2,4-diaminopyrimidinium perchlorate (**dapClO₄**), 2,4-diaminopyrimidinium nitrate (**dapNO₃**), bis(2,4-diaminopyrimidinium) selenate dihydrate (**dap₂SeO₄2H₂O**) and bis(2,4-diaminopyrimidinium) hydrogen phosphate tetrahydrate (**dap₂HPO₄4H₂O**).

2. Experimental

The products derived from 2,4-diaminopyrimidine (**dap**, Aldrich 98%) were obtained by crystallization of reaction mixtures prepared by dissolving **dap** in 20–50 mL of distilled water and adding the corresponding amount of 2 mol/L of acid solution (hydrochloric, perchloric, nitric, selenic and phosphoric). The molar ratio (base: acid) was chosen to follow the expected stoichiometry of the potential products. After slow evaporation of water at room temperature, the products were colourless crystals of **dapClH₂O** (starting molar ratio 1: 1), **dap₂ClO₄** (starting molar ratio 1: 1), **dapClO₄** (starting molar ratio 1: 2), **dapNO₃** (starting molar ratio 1: 1), **dap₂SeO₄2H₂O** (starting molar ratios 1: 1 and 2: 1), and **dap₂HPO₄4H₂O** (starting molar ratio 2: 1). The obtained crystals were filtered off and dried in air.

Single-crystal X-ray diffraction data of **dapClH₂O**, **dap₂ClO₄**, **dapClO₄**, **dapNO₃**, **dap₂SeO₄2H₂O** and **dap₂HPO₄4H₂O** were collected on a Nonius Kappa diffractometer (MoK α radiation, graphite monochromator) equipped with Bruker APEX-II CCD array detector (computing programs SAINT [26], Diamond [27], PLATON [28]). The temperature of each sample was controlled by an Oxford Cryosystems liquid nitrogen Cryostream cooler. The phase problem was solved by direct methods (SIR-97 software [29]) and the non-hydrogen atoms were refined anisotropically, using the full-matrix least-squares procedure (SHELXL-97 [30] and JANA2006 software [31] into which extinction correction by Becker & Coppens [32] is included). For all the title structures, the difference electron density maps revealed all the hydrogens. There have been tested various refinement models with different constraints and restraints regarding the hydrogens' parameters. Therefore, the treatment of the hydrogens can differ in the respective structures, nevertheless, in all the cases the aryl hydrogens were constrained with $C_{\text{aryl}}-H = 0.94 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C_{\text{aryl}})$ assuming trigonal configuration of the carrier carbon atom. The detailed refinement of hydrogen atoms in the title crystal structures is included into the [Supplementary materials](#). The basic crystallographic data, measurement and refinement details are summarized in [Table 1](#). The

selected bond lengths and angles, including those of hydrogen bonds, are presented in [Supplementary materials, Tables 1S–6S](#). Crystallographic data for **dapClH₂O**, **dap₂ClO₄**, **dapClO₄**, **dapNO₃**, **dap₂SeO₄2H₂O** and **dap₂HPO₄4H₂O** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 1406427, CCDC 1406428, CCDC 1406431, CCDC 1406432, CCDC 1406430 and CCDC 1406429, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CG21, EZ, UK (fax: (44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

The phase purity of the prepared polycrystalline samples was also controlled by powder X-ray diffraction at room temperature using the Bragg-Brentano geometry on a Philips X'pert PRO MPD X-ray diffraction system equipped with an ultra fast X'Celerator detection using Cu-anode (Cu-K α ; $\lambda = 1.5418 \text{ \AA}$). Recorded diffraction patterns (see [Tables 7S–13S; Supplementary materials](#)) are consistent with the calculated diffraction maxima (FullProf software [33]).

The infrared spectra were recorded using nujol and fluorolube mulls (KBr windows) technique on a Nicolet 6700 FTIR spectrometer with 2 cm^{-1} resolution and Happ-Genzel apodization in the $400\text{--}4000 \text{ cm}^{-1}$ region. The FAR IR spectra were recorded down to 50 cm^{-1} (4 cm^{-1} resolution, Solid Substrate™ beamsplitter, DTGS detector, Happ-Genzel apodization) in PE pellets.

The Raman spectra of the polycrystalline samples were recorded at room temperature on a Nicolet 6700 FTIR spectrometer equipped with the Nicolet Nexus FT Raman module (2 cm^{-1} resolution, Happ-Genzel apodization, 1064 nm Nd:YVO₄ laser excitation, 450 mW power at the sample) in the $150\text{--}3700 \text{ cm}^{-1}$ region.

Quantum-chemical calculation (GAUSSIAN09W [34]) of 2,4-diaminopyrimidine and 2,4-diaminopyrimidinium (1+) cation was performed employing the closed-shell restricted density functional method (B3LYP) with the 6-311+G(d, p) basis set. The visualization of the results was carried out with the GaussView [35] program package. The geometry optimizations, also yielding the molecular energies, were followed by frequency calculations together with IR intensities and Raman activities using the same method and the basis set. The optimal scaling scheme for calculated frequencies was inferred from comparison of results, which were obtained by application of WLS (Wavenumber-Linear Scale) procedure [36] and dual scaling [37] procedures with the experimental values recorded for **dap** base or **dapClH₂O**. The spectra were analysed in terms of the PED (Potential Energy Distribution) contributions by using the VEDA (Vibrational Energy Distribution Analysis) program [38]. The theoretical Raman intensities of the computed normal modes were calculated (RAINT program [39]) for 1064 nm excitation wavelength taking Raman scattering activities from the Gaussian output.

3. Results and discussion

3.1. Crystal structures

In the title structures, the most intriguing feature is the hydrogen bond pattern between 2,4-diaminopyrimidine or 2,4-diaminopyrimidinium molecules and different anions, which have a varying ability to act as hydrogen-bond acceptors. For example, the excess of the donating hydrogens in 2,4-diaminopyrimidinium chloride hemihydrate with respect to the chloride anion can be mitigated by the involvement of the water molecules into this structure.

2,4-diaminopyrimidinium has two primary amine groups involving atoms N3 and N4 as well as N1 or N2 atoms, which are part of the aromatic ring. N₁ tends to be hydrogenated in a sufficiently acid environment and N₂ can act as a hydrogen bond

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