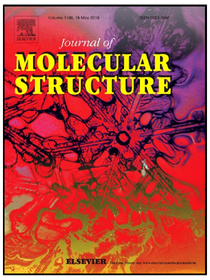

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Sulfamates and methanesulfonates of *L*-arginine and *L*-histidine

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Abstract

Reactions of *L*-arginine (*L*-Arg) and *L*-histidine (*L*-His) with sulfamic (NH_2SO_3H) and methanesulfonic (CH_3SO_3H) acids in aqueous media were investigated. The following salts (*L*-ArgH)(NH_2SO_3) (I), (*L*-ArgH)(CH_3SO_3) (II), (*L*-ArgH_2)$(CH_3SO_3)_2$ (III), (*L*-HisH)(NH_2SO_3) (IV), (*L*-HisH_2)$(NH_2SO_3)_2$ (V), (*L*-HisH)(CH_3SO_3).$2H_2O$ (VI), (*L*-HisH_2)$(CH_3SO_3)_2$ (VII) were obtained and characterized structurally and by vibrational spectroscopy. Large crystals of (II), (VI), (VII) were grown from aqueous solution by evaporation method. The crystal (IV) was known previously and characterized spectroscopically, however, the published infrared spectrum significantly differs from our spectrum.

Keywords: L-arginine; L-histidine; sulfamate; methanesulfonate; crystal structure; vibrational spectra

1. Introduction

Salts of *L*-arginine and *L*-histidine are the most studied among salts of amino acids [1]. However, methanesulfonates of *L*-arginine and *L*-histidine were not known and only spectroscopic characterization of *L*-histidinium sulfamate was reported without details of its crystal structure [2]. Crystals of betainium sulfamate (BetH)(NH_2SO_3) were grown and elastic and thermoelastic constants were measured in Ref. [3]. The authors of Refs [4,5] found that additionally a new salt with betaine betainium dimeric cation exists in this system, which was the first salt with dimeric cation of an amino acid with sulfamate anion (Bet···BetH)(NH_2SO_3). This research group also obtained and studied in detail the crystal (Sar···SarH)(CH_3SO_3) [6,7], which was the first of salts with methanesulfonate anion of an amino acid. A simple salt of glycinium methanesulfonate (GlyH)(CH_3SO_3) [8] also was obtained and investigated. All these salts crystallize in centrosymmetric structures. *L*-arginine and *L*-histidine can form salts with singly and doubly charged cations [9,10]. Additionally, being optically active, these amino acids form salts which must be noncentrosymmetric.

The aim of the present work was a more systematic investigation of salts formation in the *L*-arginine-NH_2SO_3H-H_2O, *L*-arginine-CH_3SO_3H-H_2O, *L*-histidine-NH_2SO_3H-H_2O and *L*-histidine-CH_3SO_3H-H_2O systems.

We report our results on obtaining, crystal growth, structure determination and spectroscopic characterization of sulfamate and methanesulfonate salts of *L*-arginine and *L*-histidine.

2. Experimental

2.1. Materials and synthesis

As initial reagents we used *L*-arginine (≥98.0%, TLC), *L*-histidine (≥99.0%, TLC), sulfamic acid (99.3-100.3%, ACS reagent) and methanesulfonic acid (≥99.0%) from Sigma-Aldrich Co. Crystals of the titled compounds have been obtained by slow evaporation at room temperature from aqueous solution containing a stoichiometric ratio of the respective amino acid and a sulfonic acid. The growth of several crystals was carried out by slow evaporation at constant temperature 32°C using seeds, and grown crystals have been separated after 7 days.