Novel nonlinear optical crystal of L-arginine dichloride

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The salts of optically active L–amino acids, particularly L–arginine, crystallize in enantiomorphous space groups P2₁2₁2₁, P2₁, P1, and very rarely in others. These space groups being acentric allow displaying nonlinear optical (NLO) and piezoelectric properties, while polar P2₁ and P1 groups, also have a pyroelectric effect. Search and investigation of L–arginine (L–Arg) salts as objects related to proteins began from the study of halides at the beginning of the sixties. We investigated in detail the reaction of L–arginine with hydrochloric acid (HCl) in water solvent at 0–33°C temperature [1]. In total, five compounds were successfully obtained and identified, of which L–Arg·HCl (P1) [2], L–Arg·HCl·HCl (P2₁) [3], L–Arg·HCl·H₂O (P2₁) [3], L–Arg·2HCl·H₂O (P2₁2₁2₁) [4] were known, and L–Arg·2HCl (new) crystal was a novel finding. The conditions for the formation of all obtained crystals from the L–Arg+HCl+H₂O system were described; the FT–IR ATR spectra were presented and compared in [1].

The subject of the present study is NLO novel crystal of L–Arg·2HCl (3L–Arg⁺·6Cl⁻). The crystal and molecular structure of crystal L–Arg 2HCl was determined by X-ray diffraction method at 295K. This crystalize in the monoclinic (P2₁) system. Unit cell parameters: a=7.4907(15)Å, b=20.092(4)Å, c=12.101(2)Å, α=γ=90°, β=99.35(3)°, Z=6, Dc=1.370 g/cm³, V=1797.0(6)Å³. The asymmetric part of the unit cell of L–Arg·2HCl contains crystallographically independent three L-argininium (2+) cations and six Cl⁻ anions (Fig. 1a). The guanidyl group of I or III types cations is connected to the carboxyl group of next cations of their type, that is, it forms a chain according to the “head to tail” mechanism, stretching along the c axis. And cations of II type are not directly connected to each other, they form hydrogen bonds through the own carboxyl group with the guanidyl group of III type cation, forming layers in the direction of the b axis, they are also connected through Cl⁻ anions. That is, layers of arginine cations are formed in the bc plane, and these layers are connected through Cl⁻ anions, forming strong hydrogen bonds (Fig. 1b). In [5] were divided the interactions of the guanidyl group with carboxylate and phosphate anions into four types, and only one of the 25 studied compounds were encountered a Type D interaction. In the L–Arg·2HCl structure, the interaction between the anion and the guanidyl group is very similar to the rare Type D, but the anion is Cl⁻. The crystal can show NLO properties.

Figure 1. Asymmetric part of the unit cell and hydrogen bonds of (3 L–Arg⁺·6Cl⁻) crystal


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