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Crystal structure, differential scanning calorimetric, infrared spectroscopy and theoretical studies of $C(NH_2)_2(NH)^*CH_2{=}CHCOOH$ noncentrosymmetric crystal

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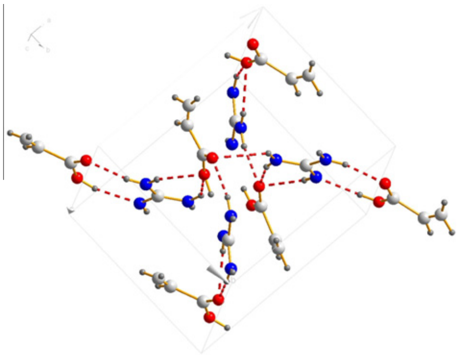
HIGHLIGHTS

- ▶ New molecular complex of guanidine and acrylic acid was synthesised.
- ▶ The second order phase transition at ca. 240 K was detected.
- ▶ On the basis of X-ray diffraction studies both phases of crystal belong to noncetrosymmetric crystallographic system.

GRAPHICAL ABSTRACT

Hydrogen bonds system in investigated crystal.



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ABSTRACT

The X-ray and vibrational spectroscopic analysis of a new molecular complex of guanidine and acrylic acid are reported. The crystal of $C(NH_2)_2(NH)^*CH_2{=}CHCOOH$ belongs to $Pna2_1$ space group of orthorhombic system with $Z = 4$, $a = 9.9242(34)$ Å, b, $c = 8.3951(14)$ Å. In the crystal structure the macroscopic symmetry center is absent.

The differential scanning calorimetric (DSC) experiment of powder sample indicates on continuous phase transition at 235.8 K.

The room temperature infrared spectrum of guanidine∗acrylic acid powder sample has been measured. The spectrum is discussed on the basis of crystallographic data. The IR spectra for the powder sample were also measured at low temperatures (12–300 K). The temperature relationships of band position for obtained spectra are analyzed.

Additionally, the results of theoretical calculation of vibrational spectra, equilibrium structure, HOMO, LUMO and first order hyperpolarizability are presented.

Introduction

For last few years a large growth of interest in "two-component" organic – inorganic compounds for non-linear optics (NLO) is noticed [1]. In this selected class of crystals belongs to the space group without macroscopic symmetry center, organic part is responsible for nonlinear optic properties while inorganic group assure the good thermo mechanical stability.

This strategy can be expanded for new group of compounds where the two organic molecules are connected by weak hydrogen interactions. In our studies the complexes are made from two compounds. The guanidine [2] molecule, as strong base, is the one part of crystal whereas the second part is built from different organic acids.

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In designing of compounds with nonlinear optical properties the special role is reserved for organic molecules with delocalized electron system. The molecules have potentially big NLO responses. On the basis of literature data [3–8] and our experience we chose the guanidinium ion as having potentially huge NLO properties. The compounds based on the guanidinium cation seem to be easy to obtain and are cheaper than chemical complexes with, for example, amino acids. The $C(NH_2)_3^+$ ion has possibility to create extensive family of complexes based on hydrogen bonds of different types. In guanidinium compounds the C—H···O and N—H···O weak hydrogen bonds are noticed very often. The N—H···O hydrogen bonds manifest in IR spectra very well as strong or medium broad bands in the range 3000–3500 cm^{-1}, whereas for C—H···O weak interactions effect of broadening of bands is not observed [9]. Additionally in some cases of C—H···O weak hydrogen bonds in infrared spectra the "blue shifting" effect is noticed [10]. In designing new crystals the weak hydrogen bonds [11] seem to play very important role both in noncentrosymmetric crystals and trigonal acentric layered structures mentioned as octupolar [12] solids.

During wide investigations some guanidinium compounds without macroscopic inverse center were found. For example the structures of diguanidinium hydrogenarsenate monohydrate [13], diguanidinium hydrogenphosphate monohydrate [14] and guanidinium maleate [15] were previously published. On the basis of experimental data or theoretical calculations of first order hyperpolarizability these compounds were classified as NLO generators [16].

Many of investigated guanidinium compounds exhibit a phase transitions, also. The phase instabilities were noticed by Szafrański et al. for many crystals of "guanidinium" family. The phase transitions were investigated for example in guanidinium halogenoplumbates [17], guanidinium trichlorostannate [18], guanidinium ethoxysulfonate [19], tetraguanidinium halogeno-sulfates [20] and guanidinium nitrate [21,22].

The new two-component complex of guanidine and acrylic acid (1:1) was obtained. The titled compound was studied using X-ray crystallography and vibrational spectroscopy. The space group of studied crystal has no macroscopic symmetry center therefore the crystal can be investigated as potential NLO generator. Additionally, the calorimetric studies of this crystal revealed the phase transition at 235.8 K.

The combination of X-ray and IR spectroscopy was used as a very useful approach for investigation of hydrogen bonds in this type of crystal. Additionally, the microscopic molecular mechanism of phase transition was investigated by IR spectroscopy at various temperatures. The influence of the hydrogen bond network of the crystal is discussed.

Experimental

The crystals of $C(NH_2)_2(NH)^*CH_2{=}CHCOOH$ were obtained by slow evaporation at constant temperature in refrigerator. The aqueous solution of guanidinium carbonate and acrylic acid was prepared in molar ratio 1:1 ($C(NH_2)_2(NH)$: $CH_2{=}CHCOOH$). Very small transparent, colorless crystals were obtained (size 1 × 1 × 1 mm approx.). It should be noticed that the crystals mentioned above were obtained in dark conditions, only. During the crystallization process at room temperature and sunlight the polymerization of acrylic acid was observed and crystal of above mentioned forms were not obtained.

The X-ray measurements were carried out on KUMA-diffraction KM-4 diffractometer with the graphite monochromator and $\omega/2\theta$ scan mode with CCD detector. The structure was solved be the direct methods (SHELX) and refined by the full-matrix least square method using SHELX program [23]. Anisotropic thermal factors were determined for all non-hydrogen atoms. The hydrogen atoms were located from the difference Fourier maps and their positions and isotropic thermal parameters were refined. All crystallographic parameters were deposited in the CCDC.

The ambient and low temperature infrared spectra were measured using the Bruker IFS-88 spectrometer with the resolution of 2 cm^{-1}. Sample, as suspension in Nujol was put between KBr windows.

Differential scanning calorimetric (DSC) measurements were performed on Perkin–Elmer DSC-7 calorimeter equipped with CCA-7 low temperature attachment with a heating/cooling rate 20 K/min. The samples of the mass ca. 20 mg were sealed in the aluminum pans. The measurements were performed in the 100–350 K temperature range.

All calculation was performed with the Firefly (PC GAMESS) version 7.1.G, build number 5618 program [24], compiled under Linux operating system. For calculations the structural data from X-ray investigations of two crystal forms were used. The coordinates for particular atoms were established and the Z-matrix was built by Molden program [25]. The Z-matrix was directly used in input Firefly files.

The optimized structures for all investigated forms of considered complex have been calculated by the DFT/B3LYP method. The 6-311++G(d,p) basis set have been employed.

The harmonic frequencies and infrared intensities were calculated by the density functional triply-parameter hybrid model (DFT/B3LYP). The 6-311++G(d,p) basis set was used. According to theoretical calculations the equilibrium structure (all positive frequencies) was obtained for studied molecule.

The Mulliken charges, HOMO and LUMO orbitals energies were analyzed directly from Firefly program log files. The graphic interpretation of mentioned properties was made by Modeling and Simulation Kit (MASK) program (version 1.3.0) [26]. In the cases of HOMO, LUMO and electrostatic potentials graphic illustrations of the isosurface with value equal to 0.01 was used.

For calculation of the first hyperpolarizability by quantum chemical time dependent Hartree Fock (TDHF) method was chosen according to procedure described in manual of Firefly program [24].

The normal coordinate analysis has been carried out for investigated molecule according to the procedure described and recommended by Fogarasi and Pulay [27]. The frequencies of C—N, N—H, C—C, C—H and C—O stretching vibrations were scaled by 0.92. The calculated potential energy distribution (PED) for the investigated molecule enabled us to make detailed band assignment in infrared spectra.

The crystal structure

At room temperature the space group of titled crystal is *Pna2₁* (orthorhombic system) with $Z = 4$, $a = 9.9242(34)$ Å and b, $c = 8.3951(14)$ Å. The detailed fractional atomic coordinates and equivalent isotopic displacement parameters were deposited in CCDC with number 873746. The structure of the crystal is shown in Fig. 1 and 2. The experimental principal bonds lengths are compared with theoretical results. These data are collected in Table 1.

The crystal comprises the branched chains of the neutral acrylic acid and guanidine molecules. These chains are created along and perpendicular to the diagonal *cb* of investigated crystal (Fig. 2). In the chains mentioned above many of different hydrogen bonds are observed. All hydrogen atoms from NH groups of guanidine molecule participate in weak hydrogen bond interactions. These bonds (six lengths) are in the range 2.77–3.15 Å. Very similar lengths of N—H···O hydrogen bonds were noticed in all investigated guanid-