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FT-IR, FT-Raman spectra and DFT calculations of melaminium perchlorate monohydrate

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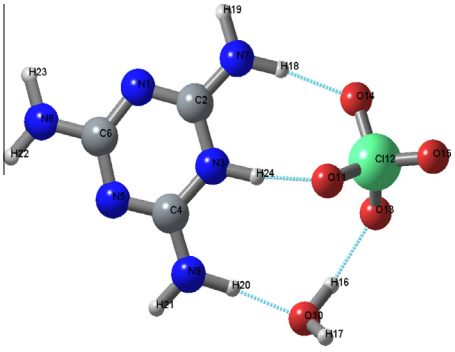
HIGHLIGHTS

- Melaminium perchlorate mono hydrate single crystals have been synthesized.
- The crystal system was identified as triclinic ($P-1$) and characterized by FT-IR, FT-Raman, FT-NMR studies.
- Several stretching and deformation modes confirm the presence of extensive intermolecular hydrogen bonding in the crystal.
- The optimized geometry and vibrational frequencies are calculated using DFT.
- HOMO–LUMO energies are calculated and show that charge transfer occurs within the molecule.

GRAPHICAL ABSTRACT



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ABSTRACT

Melaminium perchlorate monohydrate (MPM), an organic material has been synthesized by slow solvent evaporation method at room temperature. Powder X-ray diffraction analysis confirms that MPM crystal belongs to triclinic system with space group $P-1$. FTIR and FT Raman spectra are recorded at room temperature. Functional group assignment has been made for the melaminium cations and perchlorate anions. Vibrational spectra have also been discussed on the basis of quantum chemical density functional theory (DFT) calculations using Firefly (PC GAMESS) version 7.1 G. Vibrational frequencies are calculated and scaled values are compared with experimental values. The assignment of the bands has been made on the basis of the calculated PED. The Mulliken charges, HOMO–LUMO orbital energies are analyzed directly from Firefly program log files and graphically illustrated. HOMO–LUMO energy gap and other related molecular properties are also calculated. The theoretically constructed FT-IR and FT-Raman spectra of MPM coincide with the experimental one. The chemical structure of the compound has been established by ^{1}H and ^{13}C NMR spectra. No detectable signal was observed during powder test for second harmonic generation.

1. Introduction

Melamine (2,4,6-triamino-1,3,5-triazine) has wide applications in industry as a fire retardant substance. The use of melamine resin in automobile paints was examined by Zieba-Palus [1]. A lot of theoretical works were performed to explain the behavior of melamine molecule in the solid state [2–7]. Melamine complexes form the class of compounds that crystallize with interesting hydrogen-bond networks. The crystal structure of melaminium perchlorate monohydrate was published by Zhao et al. [8]. According to the data presented there, MPM consists of melaminium cat-

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ions $C_3H_7N)_6^+$, perchlorate anions ClO_4^- and water molecules. Generally, the solid state complexation of melamine with different organic and inorganic (mineral) acids has an interesting aspect concerning the hydrogen bond system formed. Such a system comprises most frequently the N–H···O and O–H···O types [4]. Generally, Spectroscopic methods are expected to provide a detailed knowledge of any molecular framework. Also they provide information on the type of symmetry present in the molecule, the nature of chemical bonds involved, the behavior of normal modes and the effect of various types of intermolecular forces. Many vibrational studies have been reported for hydrogen bonded system. A number of spectroscopic studies of melamine with inorganic acids have already been reported by Marchewka et al. [9–14]. Perchloric acid forms interesting complexes with organic cations. Perchlorates are interesting due to structural phase transition connected with the ordering of perchlorate anions [15–18]. Several researchers studied the perchlorate anion with amino acids [19–22]. In this work, we report the growth of melaminium perchlorate monohydrate (MPM). The grown crystal was characterized by X-ray diffraction. Density Functional Theory (DFT) calculations are performed in order to analyze studied molecules. The optimized structures of MPM complex have been calculated by the DFT/B3LYP method. The 6-311++G(d,p) basis set have been employed. To establish the chemical structure of MPM, NMR studies have also been carried out. The results are presented and discussed in detail.

2. Experimental

2.1. Synthesis and crystal growth

Melaminium perchlorate monohydrate ($C_3H_7N_6^+ClO_4^- \cdot H_2O$) crystals were grown by slow solvent evaporation technique. The double distilled water was used as a solvent. AR grade samples of melamine and perchloric acid were taken in 1:2 ratio. The dissolved acid was added drop wise to the hot solution of melamine. The solution was stirred well using magnetic stirrer, filtered and then allowed to cool at room temperature. Tiny, transparent, colorless crystals were grown after 3–4 weeks duration.

2.2. Characterization

The grown crystals have been subjected to various characterization studies like X-ray powder diffraction, FT-IR and FT-Raman, FT-NMR and SHG. The grown crystals have been characterized by X-ray powder diffraction technique using Rich Seifert X-ray powder diffractometer with CuK_α radiation of $\lambda = 1.5406$ Å in the 2θ range 10–70° by employing the reflection mode for scanning. The detector used was a scintillation counter. The sample was scanned at a rate of 1° min^{-1}. A Perkin Elmer Spectrum one FT-IR spectrometer was employed to record the IR spectrum to analyze the functional groups present in the crystals. The sample for this measurement was finely grounded and mixed with KBr. Raman spectral measurements were made with a FT-Raman Bruker RFS 100/S Raman module. An air cooled diode pumped Nd:YAG laser, operated at 1064 nm and a power output of 150 mW was used as source. The spectrum was recorded over the range 3500–50 cm^{-1}. Proton NMR and carbon NMR spectra were recorded using D_2O as solvent on a Bruker Avance III 500 MHz spectrometer at 22 °C to confirm the molecular structure of the grown crystal. The grown crystals of melaminium perchlorate monohydrate was subjected to Kurtz second harmonic generation test by using Nd:YAG Q switched laser beam with input pulse of 5.2 mJ for the non-linear optical property.

2.3. Computational details

All calculation were performed with the Firefly (PC GAMESS) version 7.1.G, build number 5618 program [23] compiled under Linux operating system. This job was executed on small PC Cluster consisting of three server nodes with 32-bit and 64-bit AMD processors running at 1.8 GHz and 2 GB RAM. The MPICH [24] implementation of MPI standard (Message Passing Interface) for communication between cluster nodes was used. This protocol ensures good performance and complete remote execution environment. For calculation the structural data from X-ray investigation of MPM crystal was used [8]. 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, infrared intensities and Raman activities were calculated by the density functional triply parameter hybrid model (DFT/B3LYP) with identical basis set. According to theoretical calculations, the structure with energy of form which was geometrically nearest to X-ray data, one negative frequency was obtained (see Table 4). It is clear that global minimum was not calculated [26]. Similar situation was observed in Ethylenediammonium complex [27]. The normal coordinate analysis has been carried out for investigated molecule according to the procedure described and recommended by Fogarasi and Pulay [28]. The frequencies due to stretching vibrations were scaled by 0.96. The calculated potential energy distribution (PED) for the investigated molecule has enabled us to make detailed band assignment in infrared and Raman spectra. 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) [29]. In the cases of HOMO, LUMO and electrostatic potentials graphic illustrations of the isosurface with value equal to 0.01 was used.

3. Results and discussion

3.1. Powder XRD analysis

The crystallinity was confirmed through powder X-ray diffraction analysis and from the indexed X-ray powder diffraction pattern, the unit cell parameters were calculated as $a = 5.5625 \pm 0.0765$ Å, $b = 7.7785 \pm 0.0935$ Å, $c = 11.9622 \pm 0.1560$ Å, $\alpha = 102.97 \pm 0.60°$, $\beta = 96.35 \pm 0.82°$, $\gamma = 109.26 \pm 0.69°$ and $V = 466.45$ Å^3. The calculated values agree very well with earlier literature [8].

3.2. Vibrational analysis

3.2.1. FTIR studies

The FTIR spectrum of MPM crystal is shown in Fig. 1 and the vinrational assignments are presented in Table 1. The internal vibrations of melamine molecule were already published [2–6]. According to crystallographic data, melaminium residues often form hydrogen bonds of N–H···N and N–H···O type. The bands observed in the measured region 4000–400 cm^{-1} arise from internal vibrations of melaminium cations, perchlorate anions and water molecules. The bands below 200 cm^{-1} in the Raman spectra arise from the lattice vibrations of the crystal [12]. The NH_2 theoretical stretching frequencies of neutral molecule of melamine have been determined by Fernandez-Liencres et al. [30]. NH_2 symmetric stretching of vibration occurs at 3345 cm^{-1} and generally this peak