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Synthesis and characterization of an organic material: L-histidinium glutarate monohydrate

Helen Merina Albert[1] and C. Alosious Gonsago[2]

[1]Department of Physics, Sathyabama University, Chennai, India
[2]Department of Physics, A. J. College of Engineering, Chennai, India

ABSTRACT

An organic nonlinear optical single crystal of L-histidinium glutarate monohydrate (LHG), has been synthesized by slow solvent evaporation method at an ambient temperature. Single crystal X-ray diffraction technique was employed to find the structure of the grown compound. The elemental composition of the compound was confirmed by Energy dispersive X-ray analysis. Molecular structure of LHG was established by proton NMR and carbon NMR spectral studies. The optical absorption coefficient α was analyzed from the UV spectral analysis and the optical band gap of the compound was estimated. The nonlinear optical property was confirmed by the powder technique of Kurtz and Perry.

Keywords: Organic material, XRD, EDAX, NMR, UV, SHG

INTRODUCTION

In view of the increasing demand of materials for technological applications, a continuing need persists in crystal growth development for the past few decades [1–3]. The impact of single crystals in the current technology is evident from the recent progresses in the fields of semiconductors, polarizers, transducers, ultrasonic amplifiers, infrared detectors, ferrites, magnetic garnets, solid state lasers, nonlinear optic, acousto-optic, piezoelectric, photosensitive materials and crystalline thin films for microelectronics and computer engineering. Hence, good quality single crystals are required to achieve high performance for device applications. The growth of single crystals and their characterization towards device fabrication have assumed great impetus due to their importance for both academic and applied research. In recent years, there has been significant advancement towards the investigation and growth of new class of non-centrosymmetric crystalline materials due to their substantial impact in various fields like telecommunication, optical switching, optical data storage, image manipulation and processing [4–8]. Organic nonlinear compounds find a great deal of attention, due to their potentially high nonlinearities, chemical flexibilities and rapid responses in electro-optic effect compared with the inorganic counterparts. The organic compounds with electron rich (donor) and deficient (acceptor) substituent provide the asymmetric charge distribution in the π electron system and shows large nonlinear optical responses. A number of organic materials with promising nonlinear optical characteristics have been reported recently [9–12]. Among these classes of materials, amino acids are the interesting materials for nonlinear optical applications.

The functional amino acid histidine serves as a proton donor, proton acceptor and as a nucleophilic reagent. Histidine frequently occurs at the active sites of enzymes and also coordinates ions in larger protein structures [13]. It has been observed that L-histidine could favourably form several salts with organic and inorganic acids and found that some of the L-histidine additions have second harmonic efficiency larger than potassium dihydrogen phosphate [14–17]. With the aim of obtaining new salts of L-histidine, its interactions with carboxylic acids have been studied [18, 19]. Usually, the mono-anions of dicarboxylic acids form hydrogen bonded chains [20]. These hydrogen bonds were used to construct molecular building blocks with structures in one and two dimensions. L-histidinium glutarate monohydrate has been chosen for study as a potential material for nonlinear optical applications due to its non-centrosymmetric structure. In the present work, an organic nonlinear optical crystal L-histidinium glutarate monohydrate (LHG) has been successfully grown by slow evaporation method. Spectral and optical studies are very essential methods for material characterization and hence several authors have followed these techniques for material characterization [21–24]. In this paper, we report the growth of L-histidinium glutarate monohydrate (LHG) single crystal and its characterization such as single crystal XRD, EDAX, ^{1}H NMR, ^{13}C NMR, optical absorption and SHG studies.

EXPERIMENTAL SECTION

The title compound L-histidinium glutarate monohydrate (LHG) was grown from aqueous solution by slow solvent evaporation method at room temperature. The starting material was synthesized by dissolving appropriate amounts of L-histidine (AR grade) and glutaric acid (AR grade) in deionised water taken in 1:1molar ratio. The synthesized salt of LHG was obtained by evaporating the solvent. To ensure high purity, the material was purified by repeated crystallization process, using deionized water. Recrystallized salts were taken and dissolved in deionized water at room temperature (32°C). The resulting solution was stirred well for about 8 hours and then filtered using Whatman filter paper and then allowed to evaporate at room temperature. After attaining supersaturation, tiny crystals were formed by spontaneous nucleation within 7 days. The self-nucleated tiny crystals free from macro defects were used as seeds for the bulk crystal growth. Well defined, optically transparent single crystals were obtained within a period of 30 days. The grown crystals are stable, does not decompose in air and non-hygroscopic in nature.

The crystal structure of LHG was solved using SHELXL–97 program by direct methods and refined by full-matrix least-squares on F^2 techniques. EDAX analysis was performed using FEI QUANTA 200F energy dispersive X-ray micro analyzer. In order to confirm the molecular structure of the grown crystal, FT-NMR spectral studies were carried out using the instrument Bruker 300MHz (Ultrashield) TM instrument. The UV–visible absorption study was carried out in the wavelength range of 200–1000 nmusing Varian Carry-5E UV-Vis spectrophotometer. The optical energy gap of the LHG crystal was calculated from the absorption spectrum using Tauc relation. Kurtz and Perry powder technique was employed to confirm second harmonic generation of the grown crystal.

RESULTS AND DISCUSSION

Single Crystal XRD Study

The XRD data shows that the title compound L-His$^+$·$C_5H_7O_4^-$·H_2O crystallizes in orthorhombic system with the space group $P2_12_12_1$, $Z = 4$, density = 1.412 Mg/m^3, V= 1435.88(14) Å^3. The cell parameters are a = 8.3259(5) Å, α= 90°, b = 8.8462(5) Å, β= 90°, c = 19.4953(9) Å, γ= 90°, final R_1 and wR_2 are 0.0277 and 0.0664 respectively. The crystallographic data and details of structure refinement are listed in Table 1. The ORTEP representation of LHG is shown in Figure 1. The positions of all H-atoms were geometrically generated and treated as riding on the heavier atoms to which they are bonded. All non-H atoms were anisotropically refined.

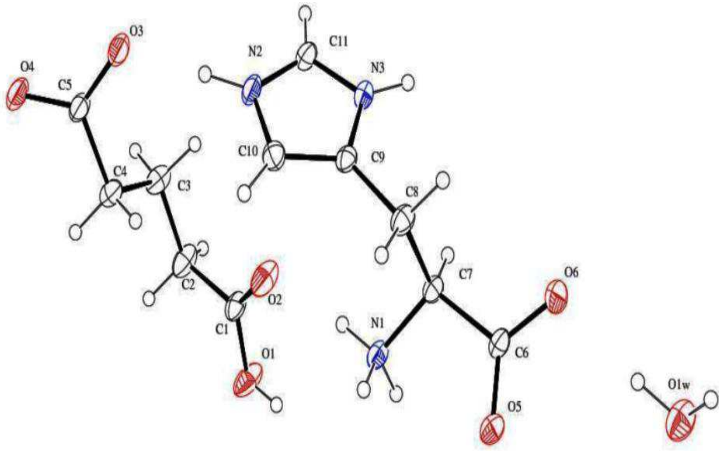

Figure 1: ORTEP representation of LHG

The asymmetric unit of the title compound consists of L-histidinium cation, glutarate anion and a water molecule linked by eight hydrogen bonds. It has been observed that L-histidinium cation contains protonated and positively charged imidazole ring, protonated amino group $(-NH_3)$ and a negatively charged deprotonated carboxyl group. Glutaric acid with two carboxylate groups exists as a single negatively charged semi-glutarate anion. In the crystal structure, the molecules are linked through inter and intramolecular N–H···O and O–H···O hydrogen bonds. There are eight polar hydrogen atoms on the title crystal fragment, three on N(1), one on each N(2), N(3), O(1) and two on O(1W) contributing hydrogen bonds. They include the O–H···O type with bond lengths varying from 2.5798 to 2.927 Å and the hydrogen bond length of N–H···O type which varies from 2.6909 to 2.9571 Å. The dimensions of all the hydrogen bonds are mentioned in Table 2. The amino group of L-histidine takes part in three hydrogen bonds, one of which has carboxylate oxygen atom O(6) of L-histidine as an acceptor. In the other two hydrogen bonds, the acceptors are the oxygen atoms O(2) and O(3) of glutarate carboxylate group. The nitrogen atoms N(2) and N(3) of imidazole ring of L-histidine takes part in hydrogen bonds with the O(4) of glutarate carboxylate group and O(5) of L-histidine carboxylate group. The water molecule forms hydrogen bonds with the O(4) of glutarate carboxylate group and O(6) of L-histidine carboxylate group. The L-histidinium cation interacts with the neighbouring glutarate anion and water moleculethrough N–H...O and O–H...O hydrogen bonds.

Table 1: Crystallographic data of LHG

Empirical formula	$C_{11} H_{19} N_3 O_7$
Formula weight	305.29
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 8.3259(5) Å, α=90° b = 8.8462(5) Å, β=90° c = 19.4953(9) Å, γ=90°
Volume	1435.88(14) $Å^3$
Z	4
Calculated density	1.412 Mg/m^3
Absorption coefficient	0.118 mm^{-1}
F(000)	648
Crystal size	0.35 × 0.30 × 0.25 mm^3
Theta range for data collection	2.53 to 24.71 deg.
Limiting indices	-9<=h<=8, -10<=k<=10, -8<=l<=22
Reflections collected/Unique	6698 / 2367 [R(int) = 0.0226]
Completeness to theta = 26.68	97.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9710 and 0.9098
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2367 / 8 / 220
Goodness-of-fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0277, wR2 = 0.0664
R indices (all data)	R1 = 0.0311, wR2 = 0.0686
Absolute structure parameter	0.3(10)
Extinction coefficient	0.0220(18)
Largest diff. peak and hole	0.166 and -0.131 $e.A^{-3}$

Table 2: Hydrogen bonding geometry for LHG

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(4)#1	0.820	1.820	2.5798(18)	153.5
N(1)-H(1C)...O(3)#1	0.930	1.799	2.7254(19)	173.8
N(1)-H(1A)...O(6)#2	0.928	1.862	2.7772(2)	166(2)
N(3)-H(3)...O(5)#3	0.909	1.855	2.6902(18)	152(2)
O(1W)-H(2W)...O(4)#4	0.921	2.302	2.927(2)	164(3)
N(1)-H(1B)...O(2)	0.919	2.047	2.9571(19)	170.5(19)
N(2)-H(2)...O(3)	0.944	1.747	2.6909(18)	178(2)
O(1W)-H(1W)...O(6)	0.932	1.880	2.8049(19)	171(2)

Energy Dispersive X-ray Analysis

Energy dispersive X-ray analysis (EDAX) is a micro-analytical tool, used to know the chemical composition of the grown compound. Highly transparent region of LHG crystal was used for the EDAX analysis. The recorded spectrum of LHG crystal is portrayed in Figure 2. The Atomic weight percentages (At%) of C, N and O as obtained from EDAX analysis are compared with the theoretical values and are listed in Table 3. The observed values are in good agreement with the theoretically calculated values and hence the formation of the title compound is confirmed by EDAX analysis.

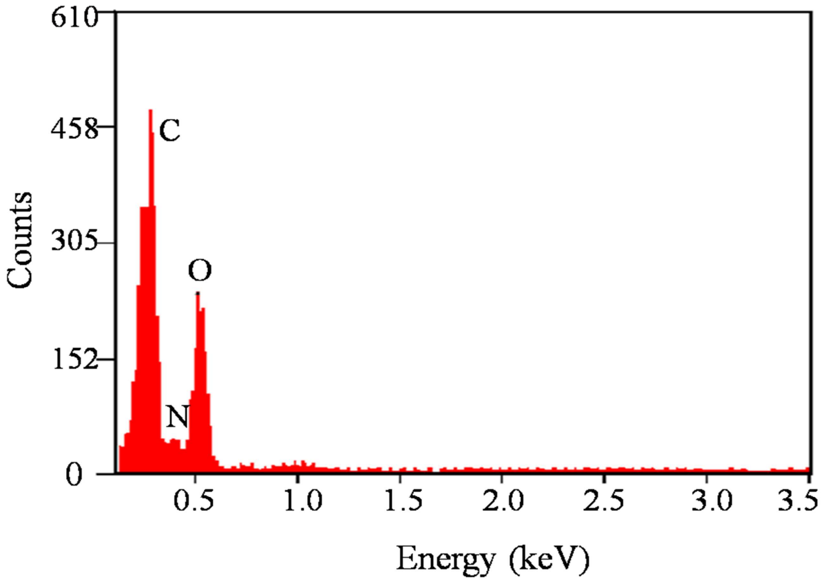

Figure 2: EDAX spectrum of LHG

Table 3: EDAX Quantification table of LHG

Element	Experimental At (%)	Theoretical At (%)
Carbon	47.14	46.17
Nitrogen	13.94	14.69
Oxygen	38.92	39.14

FT-NMR Spectral Studies

Nuclear magnetic spectroscopy provides detailed information regarding the structure, dynamics and chemical environment of molecules [25, 26]. The ^{1}H NMR spectrum of LHG was recorded at 298 K with DMSO as the solvent and is shown in Figure 3. The chemical shifts (δ ppm) are assigned and are presented in Table 4. In the ^{1}H NMR spectrum, the broad signal at δ = 12.049 ppm is due to the presence of OH group of the compound. The peaks appearing at δ = 7.692 ppm and 6.908 ppm are due to the existence of CH groups of the imidazole ring of L-histidine. The signal at δ = 4.025 ppm is due to CH(NH_2) group of the side chain of L-histidine. The broad signal around δ = 3.401 ppm is due to CH_2 group of the side chain. The triplet at 2.509 ppm and the quartet at 1.719 ppm are due to the presence of CH_2 groups of glutarate anion. The triplet at around 2.244 ppm is due to the influence of solvent DMSO.

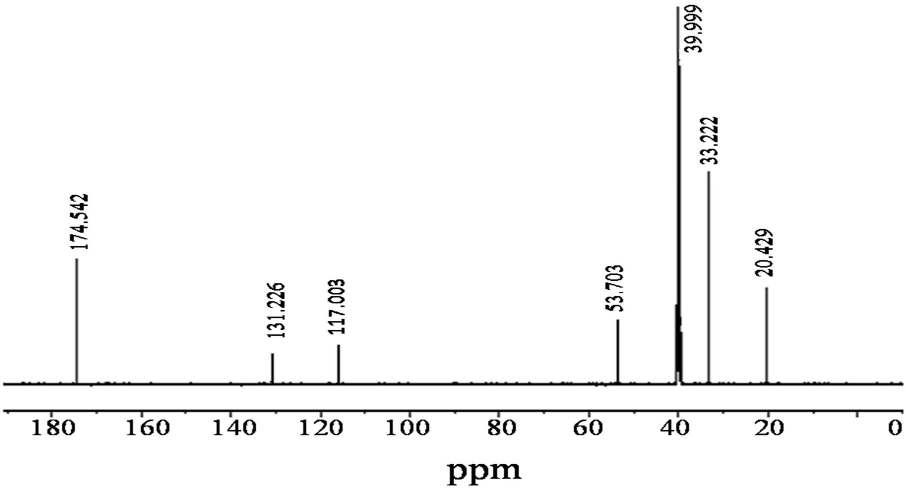

Figure 3: ^{1}H NMR spectrum of LHG

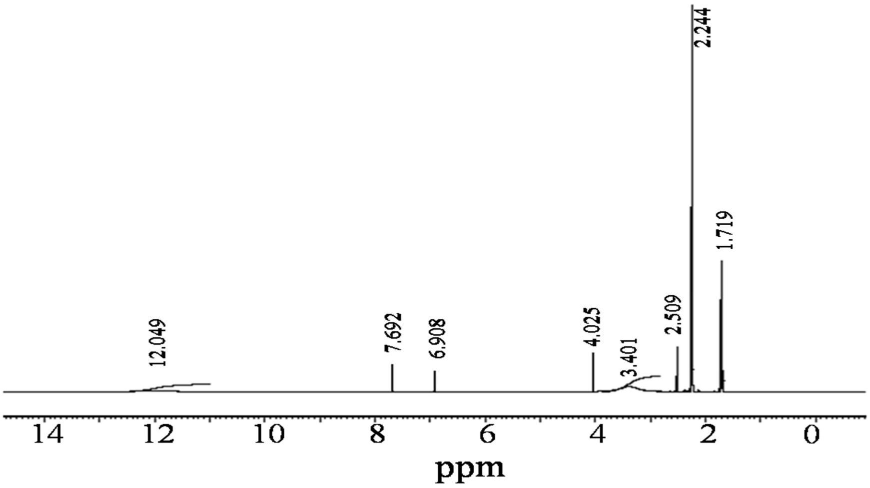

Figure 4: ^{13}C NMR spectrum of LHG

The ^{13}C NMR spectrum of LHG was recorded at 299.6 K with DMSO as the solvent and is shown in Figure 4. The peak appearing at δ = 170.896 ppm is due to CO group of glutarate anion. The peaks resolved at δ = 131.226 ppm and 117.003 ppm are due to the presence of CH groups of imidazole ring. The resonance peak appearing at δ = 53.703 ppm is due to the presence of CH group of side chain of L-histidine. The peaks resolved at δ = 20.429 ppm and 33.222 ppm are due to the presence of CH_2 group of glutarate anions. The intense peak at δ = 39.999 ppm is due to the effect of solvent DMSO.

Table 4: The chemical shifts in ^{1}H and ^{13}CNMR spectra of LHG

Spectrum	Signal atδ (ppm)	Functional groups
^{1}H NMR	1.719, 2.509	CH_2 of glutarate anion
	3.401	CH_2 of side chain
	4.025	CH of side chain
	6.908, 7.692	CH of imidazole ring
	12.049	OH group
^{13}C NMR	20.429, 33.222	CH_2 group
	39.999	DMSO (solvent)
	53.703	CH of side chain
	117.003, 131.226	CH of imidazole ring
	174.542	CO group

UV-Vis-NIR Spectral Study

The UV-Vis-NIR absorption study was performed to identify the usefulness of LHG crystal for nonlinear application in the visible and UV regions. The UV-Vis-NIR absorption spectrum was recorded for the LHG crystal in the wavelength region of 200−1000 nm using a Varian Carry-5E UV−Vis Spectrophotometer. The recorded absorption spectrum of LHG is portrayed in Figure 5. From the absorption spectrum, it is observed that the optical absorption in the grown crystal is almost negligible in the UV and visible spectral regions with the lower cut off wavelength at 235 nm. Minimum absorption in the UV–visible spectral region reveals that the LHG crystal is highly transparent and this is a much needed prerequisite for NLO applications [27].

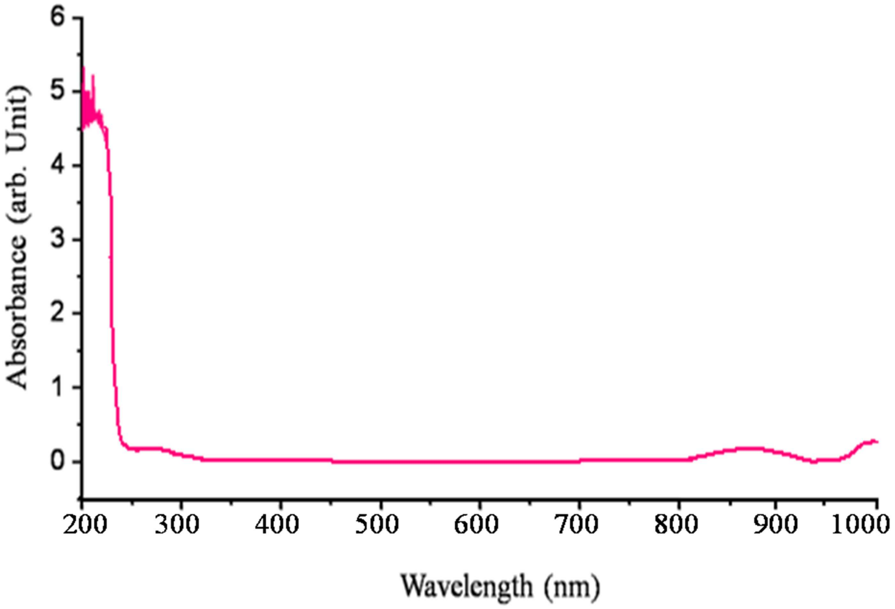

Figure 5: UV-Vis-NIR spectrum of LHG

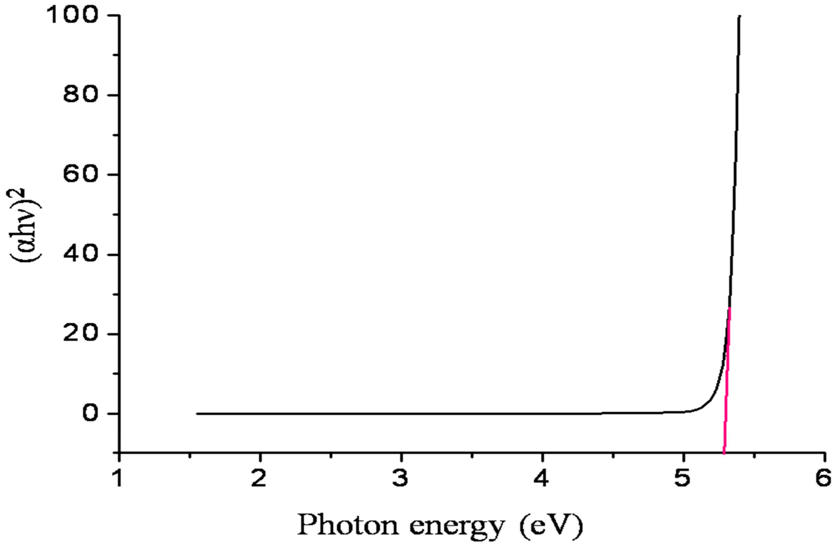

Figure 6: Band gap estimation of LHG

The UV-visible absorption study is also helpful in understanding the electronic structure of the optical band gap of the grown crystal as it strongly influences the electrical and optical characteristics of the crystal. The optical band gap of the crystal is calculated from Tauc equation. From the absorption spectrum, a curve is plotted between hν and $(\alpha h\nu)^2$and is depicted in Figure 6. The optical band gap of LHG is evaluated by drawing a straight line in the linear region of the graph at $(\alpha h\nu)^2=0$ [28, 29]. The band gap energy of LHG crystal has been evaluated from the graph and is found to be 5.25 eV.

Kurtz and Perry SHG Test

The nonlinear optical property of grown compound was tested by Kurtz and Perry powder technique [30]. In this method, the compound was grounded into fine microcrystalline powder and densely packed between two transparent glass plates. A Q-switched Nd:YAG laser operating at a fundamental wavelength 1064nm was used for this analysis. The laser beam with 8 ns pulse width and 10 Hz pulse rate was made to fall normally on the sample cell. The output beam from the sample was filtered and then displayed on the oscilloscope. The generation of second harmonic signal was confirmed by the emission of a green light (532 nm) from the sample. Powdered KDP sample was used as a reference material in the SHG measurement. It has been observed that the SHG efficiency of LHG crystal is 0.73 times that of KDP.

CONCLUSION

An organic nonlinear optical LHG single crystal was grown successfully by slow solvent evaporation method at room temperature of 32°C. Crystal structure and lattice parameters were determined by single crystal X-ray diffraction analysis using SHELXL–97 program by direct methodsand refined by full-matrix least-squares on F^2 techniques. Crystallographic data shows that LHG belongs to orthorhombic system with the space group $P2_12_12_1$. Chemical composition of LHG was established by EDAX analysis. Molecular structure of LHG was elucidated by proton and carbon NMR spectral studies. UV-Vis-NIR spectral study substantiates the optical transparency of the crystal without any significant absorption in the wavelength range 235–1000 nm, which is quite suitable for nonlinear applications in the green or blue regions. The optical band gap (E_g) of the LHG crystal was estimated and is found to be 5.25 eV. The SHG efficiency of LHG was found to be 0.73 times that of KDP.

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