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Crystal growth, spectral, optical and thermal properties of semiorganic nonlinear optical material: Picolinic acid hydrochloride

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- PHCL crystallizes in orthorhombic crystal system.
- Molecular structure was confirmed by NMR spectral analysis.
- The kinetic and thermodynamic parameters of thermal degradation process have been calculated.



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ABSTRACT

The bulk single crystal of 2-picolinic acid hydrochloride (PHCL) (a semi-organic nonlinear optical material of dimensions $25 \times 15 \times 10 \text{ mm}^3$) was successfully grown by slow solvent evaporation technique. The XRD results revealed the cell parameters and the centrosymmetric nature of the crystal structure. FT-IR spectral study identified the functional groups, nature of bonding and their bond strength. The UV–Vis–NIR studies recognized the optical transmittance window and the lower cut off wavelength of the PHCL crystal and thus it could be performed as a NLO material. ¹H NMR and ¹³CNMR spectra were correlated with the XRD standard for the molecular structure reveals harmony of the materials. Thermal properties of the crystal were studied by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA); the derived kinetic parameter values support the intuitive association of picolinicacid and HCl leads to the spontaneous formation of PHCL with a first order reaction. The presence of a proton and a proton acceptor groups provide the necessary stability to induce charge asymmetry in the PHCL structure. The load dependent hardness values of the crystal were measured by microhardness testing.

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Introduction

In the recent times the research activities are focussing on the design and development of highly efficient semi-organic nonlinear optical (NLO) materials [1]. Nonlinear optical (NLO) effect is the

* Corresponding author. Tel.: +91 9262411234. E-mail address: kavin_shri@yahoo.co.in (T. Uma Devi). atomic level response in a dielectric material to the electric fields present in an intense light beam. The propagation of a light wave through a dielectric material produces changes in the spatial and temporal distribution of electrical charges as the electrons in the atoms interact with the electromagnetic fields of the light wave. The interaction between the laser beam and the delocalised π -electrons in the organic molecule (having a π -electron conjugated system) cause nonlinear polarization. The amount of nonlinear polarization of the organic molecule can be increased when an

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Fig. 1. Chemical structure of PHCL.

electron donating group (donor) or an electron withdrawing group (acceptor) is introduced (inorganic material) into the π -electron conjugated system [2,3]. The development of functional molecular materials with desirable physical properties such as ferroelectric, ferromagnetic, photo conducting and NLO properties for practical applications has become one of the fast growing multi-disciplinary thrust research areas. The semi-organic crystals possess attractive properties such as high damage threshold, wide transparent region and a high nonlinear coefficient [4]. Many applications using NLO materials require single crystals of these materials in bulk form that could be achieved only with semi-organic crystals, which exhibit wide transparency, large and bulky crystal morphologies. The picolinic acid (pyridine 2-carboxylic acid) is very often used in NLO studies as it has the ease of protonation in acid solution [5,6]. The compound picolinic acid hydrochloride (PHCL) crystallizes in centrosymmetric space group P_{nma} having four independent molecules in the asymmetric unit. In PHCL $(C_6H_6NO_2^+,Cl^-)$ there are two strong hydrogen bonds namely OH···Cl and N-H···Cl are formed between the cations and anions as zigzag chains that are parallel to the 'a' axis. The Chemical Structure of PHCL crystal is shown in Fig. 1.

Experimental

Synthesis and growth of single crystal

The picolinic acid $C_6H_5NO_2$, and the hydrochloric acid HCl (both with AR grade purity) were obtained from Sigma. To the homogeneous solution of picolinic acid (dissolved in double distilled water), HCl is added slowly with continuous stirring until it is completely miscible and forms a homogeneous solution. The precipitates were then washed with distilled water until excess chloride ions (qualitative test with AgNO₃/HNO₃ solution) are eliminated and the remaining is maintained in an aqueous suspension.

The following reaction leads to the formation of PHCL

$$C_6H_5NO_2 + HCl \rightarrow C_6H_6NO_2^+Cl^-$$

The solutions and as well as the water employed for washing the precipitates were purged with nitrogen gas and the system was maintained in an isolated manner to avoid oxidation. The prepared solid-state compounds were maintained in aqueous suspension with 50 mL picolinic acid solution of 0.10 mol concentration, and the suspension was heated slowly to near ebullition, until the acid is totally neutralised. Any excess acid was removed by filtration and the crystals were evaporated to dryness in a water bath, subsequently dried in hot air and kept in a desiccator over anhydrous calcium chloride. Photograph of the grown PHCL single crystal is exhibited in Fig. 2.

Materials and methods

All chemicals used are of the analytical reagent grade (AR), and of the highest purity available. The solvents are obtained in spectroscopic pure form (BDH). Hydrochloric and Nitric acid (Merck)



Fig. 2. Photograph of the as-grown single crystal of PHCL.

are used along with the de-ionized water collected from an all glass equipments were generally used in all preparations.

X-ray powder patterns were obtained using Siemens D-5000 Xray diffractometer employing Mo K α radiation of λ = 1.5406 Å. The attenuate total reflectance infrared spectra for picolinic acid and its PHCL crystal were run on a Perkin–Elmer FT-IR type 1650 spectrophotometer in the wave number region from 4000 to 500 cm⁻¹. The spectra were recorded using KBr pellets. The solid reflectance spectra were measured using a Shimadzu 3101 pc spectrophotometer. Simultaneous TG–DTA curves were obtained with two thermal analysis system, model SDT 2960 from TA Instruments. The air flow of 100 mL min⁻¹ is purged for TG–DTA experiments. A heating rate of 20 °C min⁻¹ was adopted and the sample (7 mg) were kept in a alumina and aluminum crucibles, the latter with perforated cover, were used for TG–DTA.

Results and discussion

X-ray diffraction studies

The compound crystallizes in orthorhombic system with space group P_{nma} possessing the lattice parameters of a = 13.7876 Å, b = 6.5268 Å, c = 7.7517 Å and the unit cell volume V = 1232 Å³ which matches well with earlier reports [7].



Fig. 3. FT-IR spectrum of PHCL.

FT-IR Spectral studies

The characteristic bands of PHCL crystal is shown in FT-IR spectrum (Fig. 3). The characteristic vibrational bands in the spectrum were compared with the corresponding bands of picolinic acid [8]. It is observed that most of the referred bands were split or have changes in their respective band position/intensity thus indicating the mixed nature of picolinic acid and hydrochloric acid. The major vibrational modes of PHCL were derived from the pyridine ring, N—H group and C=O group. The determination of the crystal structure of mixed PHCL may help to establish definitive vibrational assignments and thus potentially able to deliver a deeper insight into mechanisms of dynamical interactions. The measured infrared band positions and their assignments are given in Table 1.

The hydroxyl group vibrations, which are hydrogen bonded to the aromatic ring π -electron systems arising bands in the range 3300–3350 cm⁻¹, in the present study, it is found that a broad band appears at 3322 cm⁻¹, also the intensity of the band was increased due to conjugation/formation of hydrogen bonds [9]. The COOH symmetric and asymmetric stretching vibrations were observed at 3092 cm⁻¹ at 3300 cm⁻¹ respectively. The N–H stretching vibrations were lowered with a red shift which serves as a sign for the –COOH group participation in the intermolecular interaction. Therefore, it could be arrived that the intermolecular hydrogen bonding is responsible for high β value and this mechanism plays an important role in NLO activity of the PHCL crystal.

The aromatic stretching exhibits multiple weak bands in the region between 3100 and 3000 cm⁻¹ and the C—H vibrations of the PHCL crystal were observed at 3092, 2857 cm⁻¹. The out-plane deformation of C—H molecules was observed at 960 cm⁻¹ which could be attributed to strong coupled vibrations [9]. The observed band positions were suppressed in frequency as it was shared its bonding electrons to the hydrogen bonding.

The unconjugated C=N linkage gives weak to medium bands near 1250–1020 cm⁻¹ because of C=N vibrations. In the present study C=N symmetric stretching was observed at 1220 and 1088 cm⁻¹ and the bending vibrations of C=N group at 547 cm⁻¹ [10]. Since, the electrons from bonding molecular orbitals were donated to the hydrogen ion, the electron density around the C=N bond was diminished and hence the stretching frequency.

The presence of picolinate ions in the PHCL crystal structures is reflected in the highly mixed bands of the C=O stretching, -OH inplane deformation and together with OH out-of-plane bending vibrations. The intensity of carboxyl band increases due to conjugation or formation of hydrogen bonds. The most important contribution of C=O stretching vibrations were found at 1609 and 1455 cm⁻¹ and the in-plane C=O deformation could be traced at

Table 1

M	leasured	infrared	band	positions	(cm ⁻¹)	Ass	ignment	for.
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Experimental	Assignment		
v _{IR} (cm ⁻¹) Picolinic acid hydrochloride	v _{IR} (cm ⁻¹) Picolinic acid		
3410br	3464w,br	O—H Stretch + N—H stretch	
3092m	3118m	Arom. C—H Stretch	
1725m	1719s	C=O stretch	
1609m	1600vs	Ring stretch	
1455m	1443m	Ring stretch + n—h i.p bend	
1311br	1309s	Ring stretch (kekuley) + C—N stretch	
1088w	1088s	Arom. C—H i.p bend	
750s	767s	Arom.C—H o.p bend + N—H i.p bend	
669s	676vs	C—C—C i.p bend	
511s	539s	C—C—C o.p bend	

750 and 669 cm⁻¹. The anti bonding electrons form the carbonyl group molecular orbital was moved toward the newly formed interaction between the systems, thus the electron density around the carbonyl group increases consequently the stretching frequency of the C=O group also increased while compared to the picolinic acid.

The bands between 1400 and 1650 cm⁻¹ in pyridine derivatives are assigned to C—C stretching modes. The bands corresponding to a strong band at 1536 cm⁻¹ in IR is attributed to the Kekule C—C stretching mode. The FT-IR activation of pyridine ring modes provides evidence for the charge transfer interaction between the donor and the acceptor group through the π -system leading to β enhancement responsible for NLO activity.

UV-Vis-NIR spectral studies

The UV–Vis transmittance spectrum was recorded with a Cary 5E UV-Vis-NIR spectrophotometer in the range of 200-1000 nm. Fig. 4 shows the optical transmission spectrum of PHCL crystal crystallized using water as solvent. It was found that PHCL crystallized using water solvent has a transmittance of 74% with a lower UV cut-off at 194 nm. A UV cut-off below 300 nm is sufficiently useful for SHG laser generation ($\lambda = 1064$ nm) or other similar applications in the blue region [11]. Further the material was found to be transparent in the wavelength range of 300-1000 nm for all radiations. Just beyond 300 nm, there is an absorption illustrated by a decrease in transmittance. This may be due to n-p* transition in the azo-methyne group. The steep decrease in transmittance at around 250 nm may be assigned to electronic excitation in COO group. As there is no change in the transmittance in the entire range 1000 nm to 300 nm, infers that the materials can find application as window in spectral instruments in those regions.

NMR spectral study

The ¹H NMR spectrum of the PHCL crystal is shown in Fig. 5a. Four distinct proton signals appeared in the spectrum, confirming the presence of four different proton environments in the crystal. The doublet centred at δ 8.76 ppm corresponds to the C3 aromatic proton of picolinic acid moiety, and appearing as a doublet due to its coupling with the neighboring C4 aromatic proton. A triplet signal centred at δ 8.66 ppm is attributed solely to the C4 aromatic proton. A doublet signal centred at δ 8.43 ppm is assigned to the C6 aromatic proton of the picolinic acid moiety. The C5 aromatic



Fig. 4. UV-Vis-NIR spectrum of PHCL.





proton appears as a triplet signal centred at δ 8.15 ppm and is due to the coupling with two aromatic protons one each on C6 and C4 carbon atoms. The N⁺—H proton and the carboxylic acid proton of picolinic acid do not appear in the spectrum owing to their labile nature. The change in the peak positions of the crystal from their parent picolinic acid confirms its association with hydrochloric acid and in the formation of the crystal.

The ¹³C NMR spectrum of the PHCL crystal is shown in Fig. 5b. The appearance of five signals in the aromatic region of ¹³CNMR spectrum confirms the molecular structure of the crystal which is arrived from ¹H NMR. The carboxylic carbon of picolinic acid moiety brings forth a signal at δ 162 ppm. The C2, C3, C4, C5 and C6 aromatic carbon of picolinic acid moiety bring forth the carbon signals at δ 148, δ 141, δ 140.9, δ 129 and δ 127 ppm respectively.

Thermal studies

TGA and DTA curves of PHCL was carried out in an atmosphere of nitrogen at a heating rate of 10 °C/min in the temperature range



Fig. 6a. Simultaneous TGA/DTG curves of PHCL.

of 30–800 °C (Fig. 6a). Thermo gravimetric analyses for the PHCL show good agreement with the theoretical formula as suggested from the substrate and reactant materials [12].

The TG suggests that decomposition occurs in two major detectable steps. The first step corresponds to an endothermic volatilization of uncoordinated water molecules. The second or third step do



Fig. 6b. Kinetic parameters of P-HCl crystal by Coats-Redfern method.



Fig. 6c. Kinetic parameters of P-HCl crystal by Horowitz-Metzger method.

Table 2Kinetic parameters calculated for PHCl crystal.

Parameter	Coats-Redfern method	Horowitz-Metzger method
Е	$9.32 imes 10^4$	$9.62 imes 10^4$
Α	$2 imes 10^1$	6.38×10^{1}
ΔS	$-5.12 imes 10^1$	$-4.37 imes 10^1$
ΔH	$8.78 imes 10^4$	$9.02 imes 10^4$
ΔG	$1.24 imes 10^5$	1.16×10^{5}
r	0.9754	0.9856

not refer to a single process but rather is reflective of two or three overlapping processes and are attributed to the removal of the picolinic acid from the crystal system. The first mass loss occurs between 27 °C and 52.5 °C and the endothermic peaks at $T_{\rm min}$ = 77.2 °C and 99.1 °C in the DTA curve are due to the

dehydration of the water molecules, showing a loss of 2.303% which closely matches with the theoretical calculation of 2.283%. After dehydration, the thermal decomposition was found to occur between 55.2 and 430 °C, in a single step with a steep mass loss of 94.4%. (calc. 94.5%) corresponding to the liberation of major organic part of the crystal system (i.e. picolinic acid) [13]. A corresponding endothermic DTA peak observed in the range of 180–230 (T_{min} = 214.9 °C) is pertinent to the decomposition of the picolinic acid. The residual part is due to the charring of chloride with carbon. A broad exothermic peak in the DTA curve at 580 and 630 °C demonstrates the burning of the expelled products.

Thermodynamic kinetic parameters

The kinetic and thermodynamic parameters of thermal degradation process were calculated using Coats–Redfern [12] and Horowitz–Metzger methods [13]. Coats-Redfern relation [12] is as follows:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left(\frac{AR}{\beta E^*}\right) - \frac{E^*}{RT}$$
(1)

where α represents the fraction of sample decomposed at time *t*, defined by:

 $\alpha = (w_0 - w_t)/(w_0 - w_\infty)$ and *w* are the weight of the sample before the degradation, and after total conversion respectively and *T* is the derivative peak temperature. β is the heating rate = dT/dt, *E* and *A* are the activation energy and the Arrhenius pre-exponential factor, respectively. A plot of $\ln \left[\frac{-\ln(1-\alpha)}{T^2}\right]$ versus 1/T gives a straight line whose slope (*E/R*) and the pre-exponential factor (*A*) can be determined from the intercept.

The Horowitz–Metzger equation [13] is illustrative of the approximation methods used. These authors derived the relation:

$$\log\left[\frac{(1-(1-\alpha))^{1-n}}{1-n}\right] = E\theta/2.303 RT_s^2 \text{ for } n \neq 1$$
(2)

when n = 1, the LHS of Eq. (2) Would be log $[-\log(1 - \alpha)]$ For a first order kinetic process the Horowitz–Metzger equation may be written in the form the following equation:

$$\log\left[\log\left(\frac{W\alpha}{W\gamma}\right)\right] = \frac{E^*\theta}{2.303 RT_s^2} - \log 2.303.$$
(3)

where $\theta = T-T_s$, $w_{\gamma} = w_{\alpha} - w$, $w_{\alpha} =$ mass loss at the completion of the reaction; w = mass loss up to time *t*. The plot of log $[\log w_{\alpha}/w_{\gamma}]$ versus θ was drawn and found to be linear from the slope of which E^* was calculated. The pre-exponential factor *A*, was calculated from the following equation:

$$\frac{E^*}{RT_s^2} = \frac{A}{\phi} \exp \frac{-E^*}{RT_s}$$
(4)

From the thermodynamic activation parameters viz., rate of reaction and rate constants, the PHCL degradation steps were assumed to follow the first order kinetics, therefore n = 1 is understood. The linearization curves of Coats–Redfern and Horowitz–Metzger methods are shown in Figs. 6b and 6c. Kinetic parameters for the decomposition stages, calculated by employing the Coats–Redfern and Horowitz–Metzger equations, are summarized in Table 2, together with the radii of metal ions. The other thermodynamic parameters such as activation energy (*E*), pre-exponential factor (*A*), entropy of activation (ΔG) of decomposition steps were also calculated.

From the results, it could be surmised that the high values of the energy of activation of the crystals reveal that the crystal is highly stable which may be due to its strong covalent bond character. The positive *G* values illustrates that the free energy of the final residue is higher than that of the initial compound and the decomposition steps are non-spontaneous implying that the crystal formation steps are spontaneous. Also, the activation parameter *G* increases significantly for the subsequent decomposition stages of the given crystal. This is due to the significantly increasing values of T_S which overrides the values of *H*. The negative values of S for the crystals indicate a more ordered and activated state of the crystal than that of the reactants. The kinetic data obtained with the above two methods are found to be in harmony with each other.

Microhardness studies

The polished surface of the of the grown PHCL crystal was subjected to static indentations (10 s duration) at room temperature in air using Leitz Weitzlar microhardness tester fitted with a Vicker's diamond pyramidal indentor. Several trials of indentation were made on the (100) plane for each load and the average value of the diagonal length (d) of the indentation marks at each of these loads were taken. Crack initiation and material chipping become significant beyond an applied load of 100 g. Indentations are made for different loads and the value of VHN was measured after averaging the number of observations.

Vickers hardness values are calculated using the formula:

$$H_v = 1.854P/d^2$$
 (5)

where P is the applied load (kg), and d is the average diagonal length of the indented impression (mm).

It was observed that Vicker's hardness number initially decreases and attains saturation with increase in load as shown in Fig. 7a.

The plot of $\ln d$ against $\ln p$ shown in Fig. 7b is found to be a straight line which is in good agreement with Meyer's law and the slope of the curve gives the value of work hardening co-efficient value (*n*). The value *n* of the grown crystal (2.78) is greater than 2, which confirms that the grown crystal is softer [14,15]and agrees very well with the experimental results, since *HV* should increase



Fig. 7a. Load vs. microhardness.



Fig. 7b. Logd vs. LogP.

with the increase of *P* if n > 2 and decrease if n < 2 [16]. The Yield strength of the material is also calculated from the formula:

$$\sigma v = H_v / 2.9\{1 - (2 - n)[12.5(2 - n)/(1 - (2 - n)^{2 - n}]\}$$
(6)

The Knoop indented impressions were approximately rhombohedral in shape. The average diagonal length (d) was considered for the calculation of the Knoop hardness number (Hk) using the relation:

$$H_k = 14.229P/d^2$$

where *P* is the applied load in kg, *d* in mm and H_k in kg/mm².

The crystals do not show any degradation in an atmosphere with relative humidity up to 70% indicating the good moisture resistance capability of the crystals and are also found to be free of any cleavage. The chemical stability and good mechanical properties of these crystals thus make it easy to cut and polish.

Conclusion

Single crystal of Picolinic acid hydrochloride (PHCL) has been grown by slow evaporation solution growth technique. The single XRD study shows that the PHCL crystal belongs to orthorhombic system with space group P_{nma} . The FT-IR spectrum reveals the presence of hydrogen bonded N—H stretching modes which may found to be the major driving force for the packing of molecules in the crystal and confirmed hydrated nature. The ultraviolet spectrum results prove the widely transparent nature of the material between 1000 and 300 nm and thus crystal can be useful for optical applications. TGA data also supports the presence of water in the crystals and the spontaneous association of picolinic acid and HCl to form PHCL crystal is authenticated by the derived Kinetic parameter values. The measured hardness is the characteristic of these layers and the increase in hardness number is due to the overall effect on the surface and inner layers of the sample.

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