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Structural, Spectral and Antimicrobial Studies on Semi-Organic 4-Carboxyanilinium Perchlorate Monohydrate Crystal

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ABSTRACT

The semi-organic crystal of 4-carboxyanilinium perchlorate monohydrate is grown by slow evaporation method at room temperature. The single crystal XRD study of title crystal ensures that the grown crystal is in $P2_1/c$ space group with monoclinic structure. The PXRD analysis shows crystalline nature of the title crystal. The various functional groups present in the crystal are analyzed by using the FT-IR and FT-Raman spectroscopy techniques. The 4- carboxyanilinium cation and perchlorate anion is linked through the hydrogen bonding network which is confirmed by both spectroscopy techniques. The optical band gap is determined by using the UV-Visible spectroscopy analyzes and this study also reveals that the grown crystal has high transparency in the entire visible region. SEM with EDX analyzes shows that the grown crystal has smooth surface and well defined shape. The elemental composition study confirms the presence of elements in the 4-carboxyanilinium perchlorate monohydrate crystal. The antimicrobial activity of title crystal was tested against the five different micro-organisms by disc diffusion method. This result reveals that the complex crystal has more antibacterial effect than the parent crystal of PABA.

Keywords: 4-carboxyanilinium perchlorate monohydrate; XRD; Antimicrobial activity; IR; Raman; SEM; EDX

INTRODUCTION

The para crystalline compound of amino benzoic acid is also called as vitamin B_x which is an essential nutrient for some bacteria [1]. It is used to treat the therapeutic effect against typhoid and rickettsial infections [2]. PABA is naturally found in foods such as wheat, rice, eggs, and molasses. This vitamin is used in cosmetic products due to its antioxidant properties. In pharmaceutical field it plays an important role to relieve the pain from headaches, nervous states [3-5]. An excess ultra-light exposure, it acts as a sunscreen against the development of skin cancer and skin burn. It has two different (α -fiber needles and β-prims) polymorphs [6,7]. The 4-aminobenzoic acid derivatives show the enhanced antibacterial, antifungal, antitumor, analgesic and anti-inflammatory activities [8]. The crystal structure of 4-carboxyanilinium perchlorate monohydrate is already reported by Athimoolam et al. [9]. In this structure hydrogen atom of perchloric acid is liberated and protonated to NH_2 group of 4-carboxyaniline and become the carboxyanilinium cation and perchlorate anion. Also the spectroscopic study of 4-carboxyanilinium chlorate and bromate was reported recently by Susindran et al. [10]. But in our knowledge, there is no report on the spectroscopy and antimicrobial studies of 4-carboxyanilinium perchlorate monohydrate semi-organic crystal. So in the present work, an attempt has been made on the growth of 4-carboxyanilinium perchlorate semi-organic crystal by slow evaporation method. The grown crystal is characterized by single crystal XRD, powder XRD, FT-IR, FT-Raman, UV-Visible spectroscopy, SEM with EDX analyzes. These results are discussed and summarized in this present work.

MATERIALS AND METHODS

Materials

4-aminobenzoic acid, perchloric acid, ethanol and deionized water were used in the crystal growth process of title compound were purchased from Sigma Aldrich Company, India.

Crystal Growth

The 4-carboxyanilinium perchlorate monohydrate semi-organic crystal is obtained from the aqueous ethanol solution of 4-aminobenzoic acid mixed with aqueous solution of perchloric acid in 1:1 stoichiometric ratio by slow evaporation technique.

Figure 1: Grown crystal of 4-carboxyanilinium perchlorate monohydrate

This solution is stirred well for 1 hour and after filtering process it is poured into the petri disc. After a period of one week bulk crystals of title compound is harvested and which is shown in Figure 1.

Experimental Details

A good quality grown crystal of 4- carboxyanilinium perchlorate was selected to carryout out the single crystal X-ray diffraction using Bruker SMART APEX CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å). The unit cell dimension and space group of the title compound were determined and which are compared with the already reported values [9]. The XPERT–PRO X–ray diffractometer with Cu Kα (λ = 1.54060 Å) radiation was used to record the powder diffraction pattern. The FT−IR vibrational spectrum was recorded by using SHIMADZU FT−IR spectrometer in the range 4000-400 cm^{-1}. Also, the FT−Raman spectrum was recorded by using the BRUKER: RFS 27 Raman spectrometer in the wavenumber range 4000-400 cm^{-1}. The optical absorption spectrum of 4-carboxyanilinium perchlorate monohydrate semi-organic crystal has been recorded with SHIMADZU−UV1800 double beam spectrometer in the wavelength range 200−1100 nm insteps of 1 nm. The surface morphology and elemental analysis has been carried out by CARLZEISS EVO18 scanning electron microscope. The antimicrobial activity of parent and its complex crystals were tested against five different kinds of micro-organisms by disc diffusion method.

RESULTS AND DISCUSSION

Single Crystal XRD

The unit cell parameters and space group of 4- carboxyanilinium perchlorate crystal was obtained by Bruker SMART APEX CCD diffractometer. Initially, these are checked with the Cambridge Structural Database (CSD) for confirmation. The report shows that the grown crystal is exactly match with already reported values [9]. The crystallographic data of grown crystal of 4- carboxyanilinium perchlorate is shown in Table 1 and is compared with already reported values [9]. The molecular structure of semi-organic 4- carboxyanilinium perchlorate monohydrate crystal is depicted in Figure 2. This study reveals that a proton of perchloric acid is liberated and protonated with 4-carboxyaniline NH_2 group which then becomes as 4-carboxyaniline cation and perchlorate anion. Also this study confirms the grown crystal crystallizes in the monoclinic system with space group $P2_1/c$.

Table 1: Crystallographic data of 4- carboxyanilinium perchlorate monohydrate crystal

Parameters	Present study	Already reported [9]
Compound Name	4- Carboxyanilinium perchlorate monohydrate	4- Carboxyanilinium perchlorate monohydrate
Empirical formula	$C_7H_8NO_2^+ \cdot ClO_4^- \cdot H_2O$	$C_7H_8NO_2^+ \cdot ClO_4^- \cdot H_2O$
Molecular formula weight	255.61	255.61
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell Dimensions	a= 7.33 Å	a=7.55 Å
	b= 19.44 Å	b= 19.39 Å
	c= 7.59 Å	c= 7.30 Å
	α=90 °	α=90 °
	β=101.4	β=101.5 °
	γ=90 °	γ=90
Volume	1058 Å³	1046 Å³

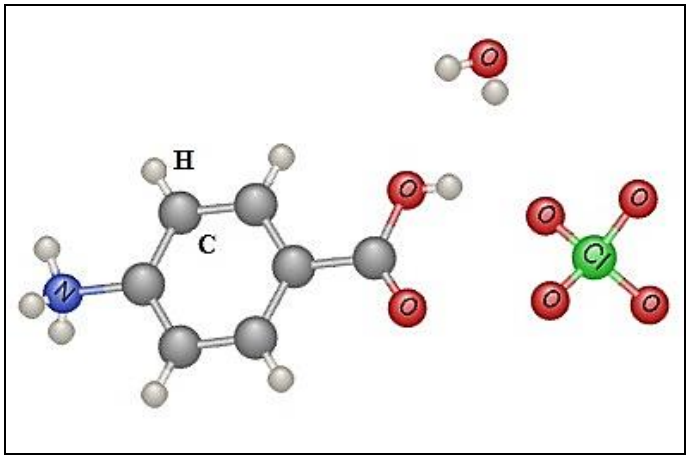

Figure 2: Molecular structure of 4-carboxyanilinium perchlorate monohydrate crystal

Powder XRD Analysis

The XPERT–PRO X–ray diffractometer is used to record the powder diffraction pattern of semi-organic crystal 4-carboxyanilinium perchlorate which is shown in Figure 3. The peaks are indexed using INDX software. The maximum number of peaks are emerged out from the XRD pattern due to the every substance in the grown material produces its own diffraction pattern. This study reveals that the good crystalline nature of title compound.

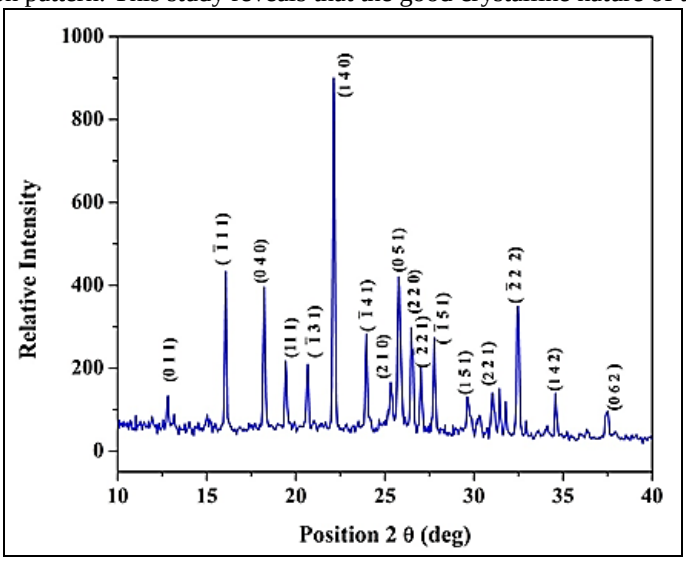

Figure 3: Diffraction patterns for 4-carboxyanilinium perchlorate monohydrate crystal

The crystalline size of the this sample was determined by using the Debye-Scherrer equation, which can be written as,

$$D = \frac{K\lambda}{\beta \cos\theta}.$$

Where,
D = crystallite size; K= dimensionless shape factor (0.94); λ = wavelength of X-ray radiation (Cu Kα = 1.54060 Å); θ = diffraction angle; β= Full width at half maximum intensity
The Dislocation density can be calculated from,

$$\delta = \frac{1}{D^2}\ m^2$$

Where,

δ Dislocation density; D is the crystallite size

The average crystalline size of 4-carboxyanilinum perchlorate monohydrate is found to be as 41 nm. The dislocation density of this semi-organic crystal is determined as $5.83 \times 10^{14}\ m^2$.

Vibrational Analysis

The semi organic crystal of 4-carboxyanilinium perchlorate monohydrate has $-[NH_3]^+$, -COOH, benzene ring, H_2O and ClO_4^- functional groups. The intensity and position of these groups are expected to change due to the presence of hydrogen bonds. The FT-IR and FT-Raman spectra of title compound are shown in Figures 4 and 5 respectively. The detailed wavenumber assignment for this compound is shown in Table 2.

Vibrations of 4-carboxyanilinum Cation

The antisymmetric and symmetric stretching mode of $-[NH_3]^+$ anilinium group is identified in the region of 3200 and 2800 cm^{-1} [11]. In the present study, $\nu_{as}-[NH_3]^+$ is identified at 3044 cm^{-1} in IR and 3084 cm^{-1} in Raman spectra respectively. Also $\nu_s-[NH_3]^+$ mode is attributed at 2922 cm^{-1} in IR and 2913,2828 cm^{-1}in Raman spectra for the title crystal. The $-[NH_3]^+$antisymmetric and symmetric deformation wavenumbers are normally expected to fall in the region 1625-1550 cm^{-1}and1550-1505 cm^{-1} respectively [11,12]. The wavenumbers are assigned at 1609 cm^{-1} and 1612 cm^{-1} in both spectra for $\delta_{as}-[NH_3]^+$ mode and 1543, 1510 (IR) cm^{-1}, 1573,1524 (Raman) cm^{-1} for $\delta_s-[NH_3]^+$ mode in the present study. The experimentally observed stretching and bending modes are deviated from the free ion $-[NH_3]^+$ due to the presence of hydrogen bonding network.

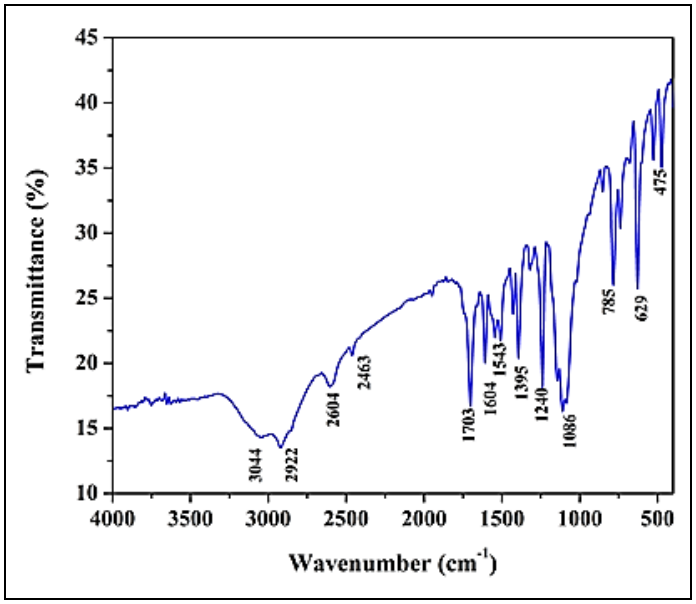

Figure 4: FT-IR spectrum for 4-carboxyanilinium perchlorate monohydrate crystal

Vibrations of Perchlorate Anion

Many authors reported the IR spectrum of perchlorate salts [13-16]. The isolated ClO_4^- ion has T_d symmetry ($\Gamma = A_1+E+2F_2$). In this symmetry, only the symmetrical stretching and bending vibrational modes (A_1 and E) are

Raman active while the antisymmetric stretching and bending vibrational modes (F_2) are both IR and Raman active. The perchlorate anion oxygen atoms form the hydrogen bond with the $[NH_3]^+$ group of 4-carboxyanilium cation which reduces the T_d symmetry of perchlorate anion to C_{2v}. In this cases, the vibrational modes are distributed as $\Gamma = 4A_1+A_2+2B_1+2B_2$. The F_2 (ν_{as}) species splits into three appearing at 1038 (A_1), 1125 (B_1) and 1170 (B_2) cm^{-1}. The A1 (ν_s) species occurs at 928 cm^{-1} while δ_{as} (F_2) wavenumber occurs at 635 (A_1), 617 (B_1) and 623 (B_2) cm^{-1}. The δ_{sym} species (E) breaks up into two bands at nearly 460 cm^{-1} (A_1, A_2). Here The A_2 species is only Raman active and the all other species are both IR and Raman active [17,18]. In this report, the antisymmetric stretching mode of ClO_4^- ion is assigned at 1144, 1111 cm^{-1} and 1086 cm^{-1} in IR spectrum for this title compound. The same group is also identified in Raman spectrum at 1068, 1112 and 1131 cm^{-1}. The symmetric stretching mode of ClO_4^- anion is assigned at 932 cm^{-1} in Raman spectrum only. The antisymmetric bending mode is observed at 637 and 629 cm^{-1} in Raman and IR spectra respectively. The symmetric bending mode is observed only in Raman spectrum at 459 cm^{-1} for title crystal. The assignments for this perchlorate anion is exactly match with earlier reported values which confirms the symmetry of perchlorate anion is C_{2v} not T_d.

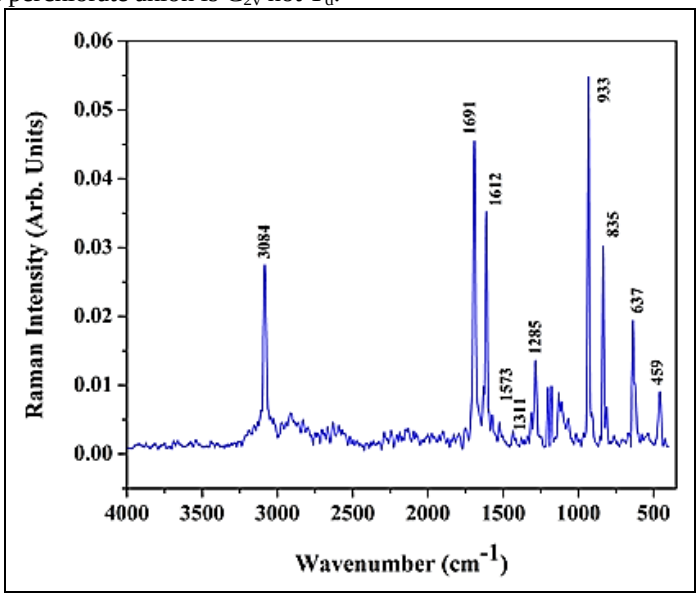

Figure 5: FT-Raman spectrum for 4-carboxyanilinium perchlorate monohydrate crystal

Vibration of Para Substituted Benzene Ring

The stretching mode of para substituted benzene ring C–H groups is expected in the region 3115 – 3005 cm^{-1} [19,20]. In an experiment, the bands observed at 3044 cm^{-1}, 3084 cm^{-1} in both spectra is assigned to ν (C–H) mode. The in–plane and out –of –plane bending vibrations of C–H are seen in the range 1250 –1000 cm^{-1} and 900 – 690 cm^{-1} respectively [19]. The β(C–H) mode is identified at 1240, 1144, 1111, 1086 cm^{-1} in FT-IR and 1131, 1112, 1068, 1014 cm^{-1} in FT-Raman spectra respectively. The γ(C–H) mode is observed in IR spectrum only at 785, 739 cm^{-1}. The C=C and C-C ring stretching modes are observed between the region 1650−1430 cm^{-1} and 1400−1300 cm^{-1} respectively [21]. For the title compound ν (C=C) mode is assigned at 1609, 1543, 1510, 1427 cm^{-1} in IR and 1612, 1573, 1524, 1435 cm^{-1} in Raman spectra. Also ν (C-C) mode is observed at 1319 cm^{-1}, 1395 cm^{-1} in IR spectrum. The C-N stretching mode is identified at 1319 cm^{-1}, 1312 cm^{-1}in both spectra for this title compound. The ring breathing mode is identified at 854 cm^{-1} in IR and 835 cm^{-1} in Raman spectra for the title compound.

Vibrations of Carboxylic Group

The antisymmetric and symmetric stretching wavenumbers of C=O group have IR band in the region 1720 - 1680 cm^{-1} and 1680-1640 cm^{-1} respectively [22]. In the present study, the absorbance bands occurs at 1794, 1751 cm^{-1} in Raman is assigned to ν_{as} (C=O) mode. Also, bands at 1703 cm^{-1} in IR and 1691 cm^{-1} in Raman is assigned to the ν_s(C=O) mode. The ν (C-O) mode of carboxylic group normally occurs in the vibrational region of 1320–1210 cm^{-1} [23]. The title compound has the wavenumbers at 1319, 1240 cm^{-1} in IR and, 1312, 1286 cm^{-1} in Raman spectra is attributed to ν (C-O) mode. The O–H stretch from CO–OH group is identified at 3065–2826 cm^{-1}. It is attributed at 3044, 2922 cm^{-1} in IR and 3084, 2913, 2828 cm^{-1}in Raman spectra respectively for title compound. The in- plane and out -of plane bending wavenumbers of O–H group appears in the region between 1440–1395 cm^{-1} and 960–875

cm^{-1} respectively [22,23]. In the present work, β(O–H) mode is observed at 1427, 1395 cm^{-1} in IR and 1435 cm^{-1} in Raman spectra. Also γ(O–H) mode is attributed only at 932 cm^{-1} in Raman spectrum of title compound.

Table 2: Wavenumber assignments for 4-carboxyanilinium perchlorate monohydrate semi-organic crystal in FT – IR and FT – Raman spectra

FT – IR ($\bar{\upsilon}$ / cm^{-1})	FT− Raman ($\bar{\upsilon}$ / cm^{-1})	Assignment
3044 (s, br)	3084 (s)	$\nu_{as}[NH_3]^+$; ν (C-H); ν (O-H)
2922(s)	2913(w)	$\nu_{s}[NH_3]^+$; ν (O-H)
-	2828(w)	ν (O-H)
-	1794(w)	ν_{as} (C=O)
-	1751(m)	ν_{as} (C=O)
1703(s)	1691(s)	ν_{s} (C=O)
1609(m)	1612(s)	ν (C=C); $\delta_{as}[NH_3]^+$
1543(s)	1573(m)	$\delta_{s}[NH_3]^+$; ν (C=C)
1510(m)	1524(m)	ν (C=C); $\delta_{s}[NH_3]^+$
1427 (w)	1435(w)	ν (C=C); β(O-H)
1395(m)	-	ν (C-C); β(O-H)
1319(w)	1312(m)	ν (C-C); ν (C-O); ν (C-N)
1240(s)	1286(s)	ν (C-O); β(C-H)
1144(m)	1131(s)	β(C-H); $\nu_{as}(ClO_4)^-$
1111(m)	1112(m)	β(C-H) ; $\nu_{as}(ClO_4)^-$
1086(m)	1068(w)	β(C-H) ; $\nu_{as}(ClO_4)^-$
-	932(s)	β(C-H); $\nu_{s}(ClO_4)^-$; γ(O–H)
854(w)	835(s)	Ring breathing
785(m)	-	γ(C-H)
739(w)	-	γ(C-H)
629(m)	637(m)	$\delta_{as}(ClO_4)^-$
-	459(m)	$\delta_{s}(ClO_4)^-$

w–weak; s– strong; m– medium;υ– stretching; υ_s– symmetric stretching; υ_{as}–anti symmetric stretching; δ_s- symmetric bending; δ_{as}- antisymmetric bending; γ– out–of–plane bending; β– in–plane bending

Optical Analysis

The absorbance spectrum of 4-carboxyanilinium perchlorate monohydrate crystal is obtained by using SHIMADZU−UV1800 double beam spectrometer in the wavelength range 200−1100 nm. The experimentally recorded absorbance spectrum is shown in Figure 6. It is shows that the crystal has the maximum absorbance peaks at 220 nm and 290 nm. The lower cut-off wavelength is found to be at 374 nm. The title crystal has 100% transmittance in the entire visible region which makes usefulness of this material in optical application. The energy gap E_g is determined by using the Tauc's relation $(\alpha h\nu)^2 = A(h\nu - E_g)$ by plotting the $(\alpha h\nu)^2$ Vs photon energy and extrapolate the linear portion of $(\alpha h\nu)^2$ to the photon energy axis gives the energy gap value of 4-carboxyanilinium perchlorate monohydrate crystal. It is found at 6.14 eV from the Figure 7.

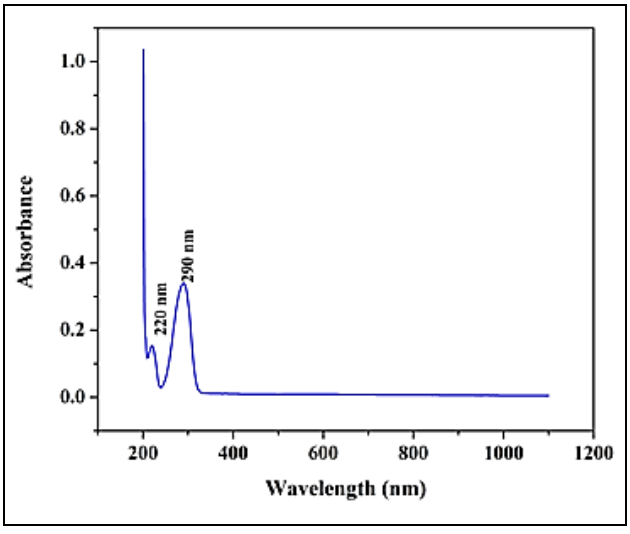

Figure 6: Absorbance spectrum for 4-carboxyanilinium perchlorate monohydrate crystal

Morphology and Elemental Analyzes

The morphology and elemental analyzes were performed by SEM with EDX analyzes. The microphotograph of title crystal is depicted in Figure 8. This image reveals that the grown crystal has a smooth surface and well defined shape.

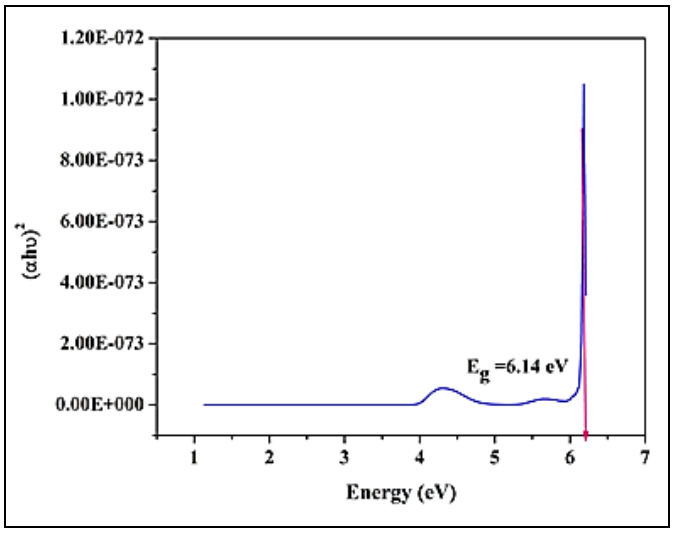

Figure 7: Optical band gap for 4-carboxyanilinium perchlorate monohydrate crystal

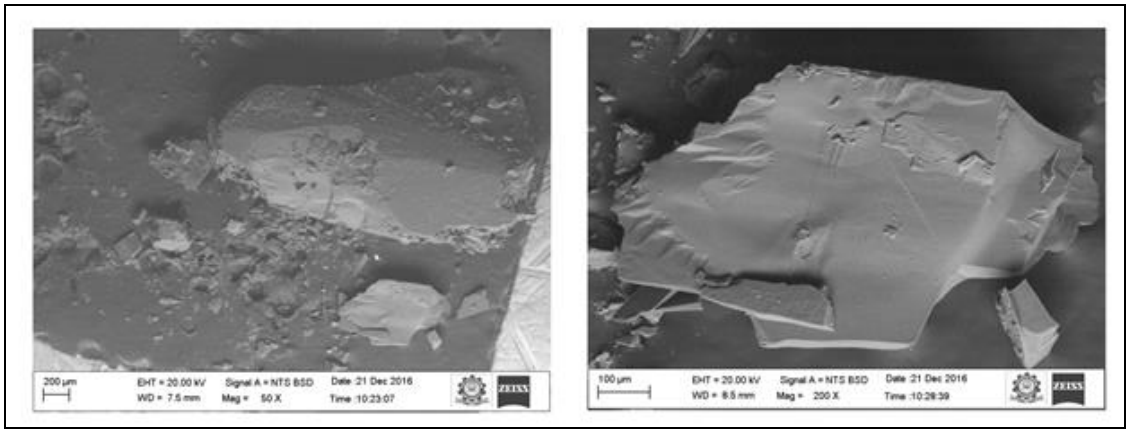

Figure 8: SEM photograph for 4-carboxyanilinium perchlorate monohydrate crystal

The EDX chart for 4-carboxyanilinium perchlorate monohydrate semi-organic crystal is shown in Figure 9. The composition of element present in crystal is shown in Table 3.

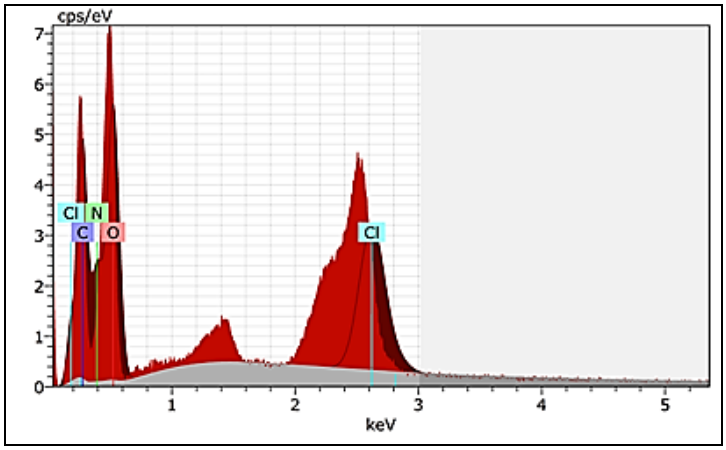

Figure 9: EDX chart for 4-carboxyanilinium perchlorate monohydrate crystal

Table 3: Elemental composition for 4-carboxyanilinium perchlorate monohydrate crystal

Elements	4-caboxyanilinium perchlorate monohydrate	
	Atomic%	Weight %
C	33.08	26.72
N	25.68	24.19
O	37.64	40.5
Cl	3.6	8.59

The elemental distribution analysis reveals that C, N, O and Cl elements are present in the grown crystal.

Antimicrobial Activity Study

The disc diffusion method is used to analyze he antimicrobial activity of 4-carboxyaniline parent and 4-carboxyanilinium perchlorate monohydrate complex crystals. They are tested against *Staphylococcus aureus*, *Proteus vulgaris*, *Escherichia coli*, *Bacillus subtilis* and *Escherichia coli* microorganisms. The photographic view of bacterial screening for parent and its complex crystals are shown in Figure 10.

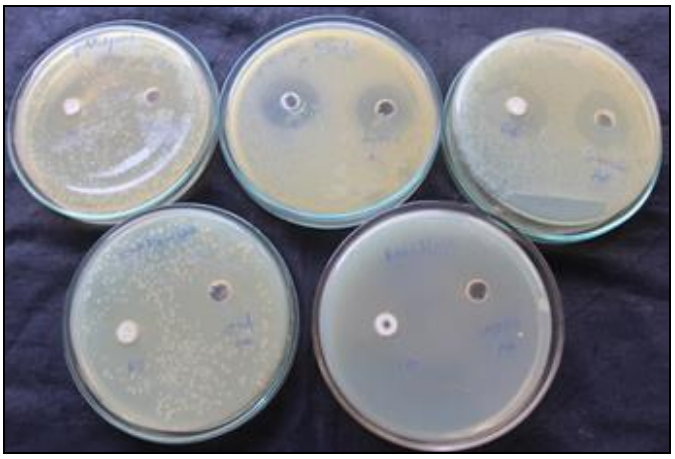

Figure 10: Photographic view of five different micro-organism activities against 4- caboxyanilinium perchlorate monohydrate crystal

The measured values of zone of inhibition for five different microorganisms of both crystals are shown in Table 4. This shows that the synthesized complex crystal is found to have more potential than pure PABA crystal against the *Proteus vulgaris*, *Escherichia coli* and *Escherichia coli*. However, the activity of complex crystal against *Staphylococcus aureus* is less than pure PABA crystal. Both crystals have no effect on *Bacillus subtilis* micro-organism. Moreover, this study concludes that the presence of chlorine atom in crystal increase the antimicrobial activity especially against *Proteus vulgaris*, *Escherichia coli* and *Escherichia coli* than *Staphylococcus aureus*.

Table 4: Effective values of inhibited zone for 4- carboxyanilinium perchlorate monohydrate crystal

S NO.	Micro-organisms	Zone of Inhibition in mm (50µl)	
		4-Carboxyaniline	4- Carboxyanilinium perchlorate monohydrate
1	*Staphylococcus aureus*	14	13
2	*Proteus vulgaris*	15	20
3	*Escherichia coli*	13	16
4	*Bacillus subtilis*	NIL	NIL
5	*Escherichia coli*	12	14

CONCLUSION

The 4-carboxyanilinium perchlorate monohydrate semi-organic crystal was grown successfully by slow evaporation method. The crystal structure is analyzed by single crystal XRD study. In PXRD analyzes the diffraction peaks are indexed using INDX software and also the average crystalline size of grown crystal is found to be as 41 nm. Using UV-Visible spectroscopy analyzes the optical band gap is determined as 6.14 eV. This large band gap shows that the grown crystal is a typical of dielectric material. The complex crystal has smooth surface and well defined shape morphology. The EDX analyzes confirms the presence of all elements of the compound present in the molecule of

title crystal. The antimicrobial activity of pure and complex crystals is analyzed by disc diffusion method which suggests that 4-carboxyanilinium perchlorate monohydrate semi-organic crystal can be used as an active substance to enhance the bacterial inhibition over PABA.

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