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Research Article

Growth and Characterization of 4-carboxyanilinium Dihydrogen Phosphate Semi-organic Complex Crystal

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Abstract

Background and Objective: The crystal structure of title compound (4-Carboxyanilinium Dihydrogen Phosphate) was already reported. But in the best of the knowledge, there is no report on spectroscopy and antimicrobial activity studies of this compound. So objective of study was to grow the 4-carboxyanilinium dihydrogen phosphate complex crystal from slow evaporation technique and characterized by single crystal XRD, powder XRD, FTIR, FT-Raman, UV-Visible spectroscopy, SEM with EDX and antimicrobial activity studies. **Materials and Methods:** The title crystal (4-Carboxyanilinium Dihydrogen Phosphate Semi-Organic Complex Crystal) was obtained by slow evaporation technique from the aqueous ethanol solution of 4-aminobenzoic acid and orthophosphoric acid in 1:1 stoichiometric ratio. In this crystal growth process, 4-aminobenzoic acid, orthophosphoric acid, ethanol and deionized water were used as the raw materials which were purchased from Sigma Aldrich Company, India. **Results:** The crystal lattice parameters and space group was obtained from the single crystal XRD study. The powder X-ray diffraction peaks were indexed using the INDX software. The FTIR and FT-Raman spectra of 4-carboxyanilinium dihydrogen phosphate crystal have been recorded at room temperature. The spectra were interpreted in terms of these wavenumber assignments. The optical band gap was determined from the UV-Visible spectroscopy analysis. Also, the morphology and antimicrobial activity studies were performed on the title crystal. **Conclusion:** The title crystal has monoclinic crystal system with the space group $P2_1/n$. The average crystalline size is found to be as 54 nm. Further, the presence of functional groups and elements were verified using FTIR and FT-Raman spectroscopy and energy dispersive X-ray studies. The SEM analysis shows that the complex crystal has smooth surface and flower like morphology. The optical band gap is determined as 3.8 eV. The antimicrobial activity study shows that the complex crystal screened the bacteria than that of the parent crystal. This modified chemical structure may improve the solubility and reduce the toxicity of drug compound.

Key words: 4-carboxyanilinium dihydrogen phosphate, XRD, FTIR, FT-Raman, SEM, EDX, antimicrobial activity

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

A cyclic amino acid compound of p-aminobenzoic acid is also known as B10 which cannot be synthesized by human¹. It is present in foods naturally and it is produced by essential symbiotic bacteria to metabolize constantly in the human body²⁻⁴. P-carboxyaniline (4-aminobenzoic acid) is an important biological molecule which has an anticoagulant and antioxidant properties. The active sites of several biological systems have kind of hydrogen bonding in hybrid compounds⁵. Due to the interest in the field of new materials and medicine, the crystal structures of organic-inorganic hybrid materials have been extensively investigated⁶. The crystal structures of 4-carboxyanilinium dihydrogen phosphate and 4-carboxyanilinium hydrogen sulfate have been already reported by Benali-Cherif *et al.*^{7,8} in which the organic bases and phosphoric acid occur in its crystalline form. In these structures, the transfer of a proton from the inorganic acid leads to protonation on the NH₂ site of the bacterial vitamin 4-aminobenzoic acid and forms the 4-carboxyanilinium cation. The crystal structures of 4-carboxyanilinium nitrate, perchlorate monohydrate and bis (4-carboxy phenyl ammonium) sulfate were reported by Athimoolam and Natarajan⁹. Susindran *et al.*¹⁰, reported the spectroscopy study of 4-carboxyanilinium chlorate, bromate crystals. Also Muthuselvi *et al.*¹¹, reported recently the vibrational and antimicrobial activity studies of 4-carboxyanilinium perchlorate monohydrate. But there is no report on the spectroscopy and antimicrobial studies of 4-carboxyanilinium dihydrogen phosphate crystal with our knowledge. So in the present investigation, an attempt has been made on the growth of 4-carboxyanilinium dihydrogen phosphate crystal by slow evaporation technique. The characterization was performed using single crystal XRD, powder XRD, FTIR, FT-Raman, UV-Visible spectroscopy, SEM with EDX and antimicrobial activity studies for the title crystal and these results are summarized in the present study.

MATERIALS AND METHODS

The 4-aminobenzoic acid, orthophosphoric acid, ethanol and deionized water were used in the crystal growth process of title compound and they were purchased from Sigma Aldrich Company, India. The single crystal of 4-carboxyanilinium dihydrogen phosphate was obtained by slow evaporation technique at room temperature from the aqueous ethanol solution of 4-aminobenzoic acid mixed with aqueous solution of orthophosphoric acid in 1:1 stoichiometric ratio. This solution was stirred well for 1 h and

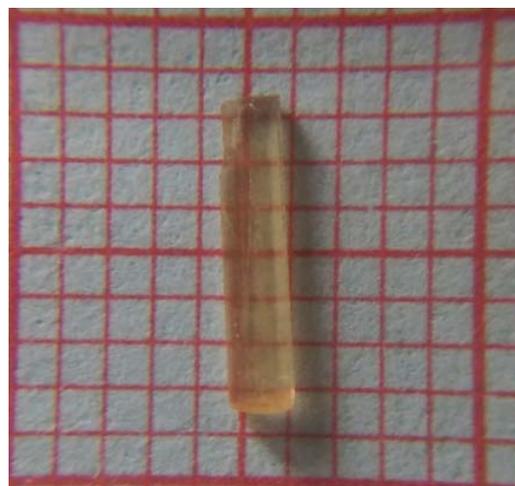


Fig. 1: Grown crystal of 4-carboxyanilinium dihydrogen phosphate

after filtering process it was poured into the petri disc. After a period of 15 days, rod like crystals of title compound was harvested and which is shown in Fig. 1. The single crystal Bruker SMART APEX CCD X-ray diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) was used to carry out the unit cell dimension and space group. This data was taken from SAIF, IIT Madras, Chennai, Tamil Nadu, India. The XPERT-PRO X-ray diffractometer with Cu K α ($\lambda = 1.54060 \text{ \AA}$) radiation was used to record the powder diffraction pattern in CSIR-CECRI, Karaikudi, Tamil Nadu, India. The FTIR vibrational spectrum was recorded using SHIMADZU FTIR spectrometer in the range 4000-400 cm^{-1} . Also, the FT-Raman spectrum was recorded in SAIF, IIT Madras, Chennai using the BRUKER: RFS 27 Raman spectrometer in the wavenumber range 4000-400 cm^{-1} . The optical absorption spectrum of 4-carboxyanilinium dihydrogen phosphate crystal has been recorded with SHIMADZU-UV1800 double beam spectrometer in the wavelength range 200-1100 nm in steps of 1 nm at V.H.N.S.N. College, Virudhunagar, Tamil Nadu, India. The surface morphology and elemental analysis has been carried out by CARLZEISS EVO18 scanning electron microscope at CSIR-CECRI, Karaikudi, Tamil Nadu, India. Using the disc diffusion method, the antimicrobial activity of parent and its complex crystals were tested against 4 different kinds of microorganisms in Sri Kaliswari College, Sivakasi, Tamil Nadu, India.

RESULTS AND DISCUSSION

Single crystal XRD: The unit cell parameter and space group of 4-carboxyanilinium dihydrogen phosphate crystal was

obtained using the SMART APEX CCD area detector diffractometer. Initially, these are checked with the Cambridge Structural Database (CSD) for confirmation. The report shows that the title crystal was exactly matched with already reported values⁷. The crystallographic data of 4-carboxyanilinium dihydrogen phosphate crystal is shown in Table 1 and was compared with already reported values⁷. The molecular structure of title crystal is illustrated in Fig. 2. The single crystal XRD study revealed that the grown crystal was a complex one, since the one proton of phosphoric acid

was liberated and joined with 4-carboxyaniline NH₂ group, then it becomes as 4-carboxyaniline cation and dihydrogen phosphate anion. Also this study confirmed the grown crystal crystallizes in the monoclinic system with space group P2₁/n.

Powder XRD analysis: The powder X-ray diffraction patterns of 4-carboxyanilinium dihydrogen phosphate crystal is shown in Fig. 3 which was recorded using XPERT-PRO X-ray diffractometer with Cu K α ($\lambda = 1.54060 \text{ \AA}$) radiation from 10 to 80° at 10°/sec scan step time. The diffracted peaks are indexed using INDX software. The good crystalline nature and purity of the grown crystal was observed from the

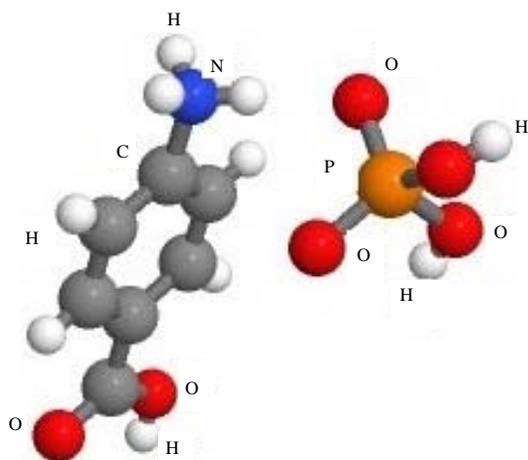


Fig. 2: Molecular structure of 4-carboxyanilinium dihydrogen phosphate

Table 1: Crystallographic data of 4-carboxyanilinium dihydrogen phosphate crystal

Parameters	Present study	Already reported ⁷
Compound name	4- Carboxyanilinium dihydrogen phosphate	4- Carboxyanilinium dihydrogen phosphate
Empirical formula	C ₇ H ₈ NO ₂ ⁺ ·H ₂ PO ₄ ⁻	C ₇ H ₈ NO ₂ ⁺ ·H ₂ PO ₄ ⁻
Molecular formula weight	235.13	235.13
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /n	P2 ₁ /n
Unit cell Dimensions	a= 6.52 (3) Å b= 22.98 (5) Å c= 7.42 (3) Å $\alpha=90^\circ$ $\beta=112.10 (2)^\circ$ $\gamma=90^\circ$	a= 6.34 (2) Å b= 22.88 (7) Å c= 7.38 (2) Å $\alpha=90^\circ$ $\beta=111.11(2)^\circ$ $\gamma=90^\circ$
Volume	988.74 (3)Å ³	998.88 (5)Å ³

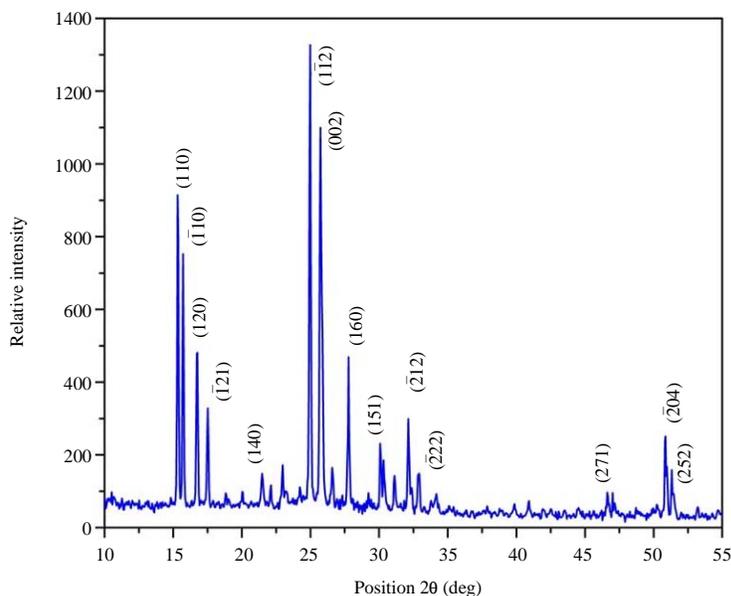


Fig. 3: Diffraction patterns for 4-carboxyanilinium dihydrogen phosphate crystal

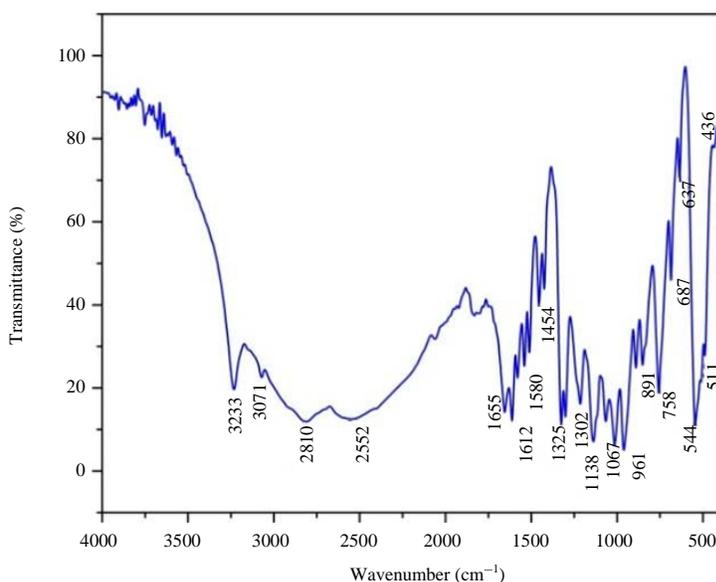


Fig. 4: FTIR spectrum for 4-carboxyanilinium dihydrogen phosphate crystal

sharp intensity PXRD pattern. The Debye-Scherrer equation was used to determine the average crystalline size of 4-carboxyanilinium dihydrogen phosphate crystal, which can be written as:

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

Where,

D = Average crystallite size

K = Dimensionless shape factor (0.94)

λ = Wavelength of X-ray radiation (Cu $K\alpha=1.54060\text{\AA}$)

θ = Diffraction angle

β = Full width at half maximum intensity

The dislocation density can be calculated from, following formula:

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

Where,

δ = Dislocation density,

D = Crystallite size

For the 4-carboxyanilinium dihydrogen phosphate crystal, the average crystalline size is found to be as 54 nm. The dislocation density of this crystal is determined as $3.43 \times 10^{14} \text{m}^{-2}$.

Vibrational analysis: The FTIR and FT-Raman spectra of 4-carboxyanilinium dihydrogen phosphate complex crystal are shown in Fig. 4 and 5, respectively and their corresponding IR and Raman assignments are listed in Table 2. The title compound has $-\text{[NH}_3\text{]}^+$, $-\text{COOH}$, para substituted benzene ring and H_2PO_4^- functional groups.

$-\text{[NH}_3\text{]}^+$ cation vibration: Normally, $-\text{[NH}_3\text{]}^+$ group has C_{3v} symmetry in the free state with a pyramidal structure. The normal modes of vibrations of this group occurs as ν_1 (A_1), ν_2 (A_1), ν_3 (E) and ν_4 (E)¹². Among these vibrations, the symmetry stretching and bending modes (ν_1 and ν_2) are non-degenerate whereas the antisymmetric stretching and bending modes (ν_3 and ν_4) are doubly degenerated. All these modes are both IR and Raman active¹². The antisymmetric and symmetric stretching modes of $-\text{[NH}_3\text{]}^+$ group are expected in the region of 3200 and 2800 cm^{-1} , respectively^{12,13}. Also, the antisymmetric and symmetric deformation modes are expected to appear in the region of 1660-1610 and 1550-1480 cm^{-1} , respectively¹³. The $-\text{[NH}_3\text{]}^+$ antisymmetric stretching wavenumber of title crystal was observed as strong band at 3233 cm^{-1} in IR and as a weak band at 3226 cm^{-1} in Raman spectra and the stretching wavenumber of this group was identified at 2810 cm^{-1} (IR), 2831 cm^{-1} (Raman), respectively.

The antisymmetric bending mode was identified at 1655 cm^{-1} , 1612 cm^{-1} in IR and at 1649 cm^{-1} , 1616 cm^{-1} in Raman spectra for the title compound, respectively. Also, symmetric bending mode was attributed at 1580 cm^{-1} ,

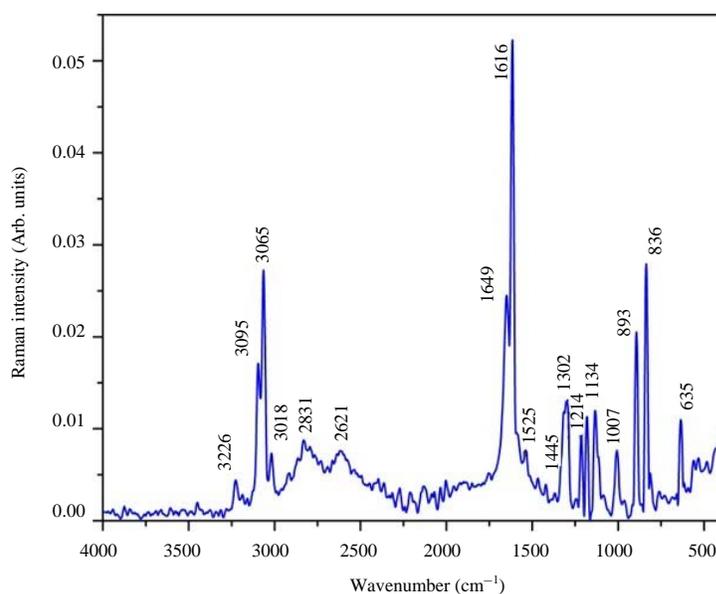


Fig. 5: FT-Raman spectrum for 4-carboxyanilinium dihydrogen phosphate crystal

Table 2: Wavenumber assignments for 4-carboxyanilinium dihydrogen phosphate crystal in FTIR and FT-Raman spectra

FTIR ($\bar{\nu}$ cm ⁻¹)	FT-Raman ($\bar{\nu}$ cm ⁻¹)	Assignment
3233 (s)	3226 (w)	ν_{as} [NH ₃] ⁺
-	3095 (m)	ν (O-H), ν (C-H)
3071 (s)	3065 (m)	ν (C-H), ν (O-H)
-	3018 (w)	ν (O-H), ν (C-H)
2810 (s, br)	2831 (w)	ν_s [NH ₃] ⁺ , ν (O-H)
1655 (s)	1649 (m)	δ_{as} [NH ₃] ⁺ , ν_{as} (C=O)
1612 (s)	1616 (s)	δ_{as} [NH ₃] ⁺ , ν (C=C), ν_s (C=O)
1580 (m)	-	δ_s [NH ₃] ⁺ , ν (C=C)
1541 (m)	1525 (w)	δ_s [NH ₃] ⁺ , ν (C=C)
1512 (m)	-	ν (C=C)
1454 (m)	1445 (w)	β (O-H)
1425 (m)	1435 (w)	β (O-H)
1325 (s)	1324 (w)	ν (C-C), ν (C-O), ν (C-N)
1302 (s)	1302 (m)	ν (C-C)
1215 (s)	1214 (m)	ν (C-O), β (C-H), β (P-OH)
1185 (m)	1182 (s)	β (C-H), ν (P=O)
1138 (s)	1134 (s)	β (C-H), ρ [NH ₃] ⁺ , ν_{as} [H ₂ PO ₄] ⁻
1067 (m)	-	β (C-H), ν_{as} [H ₂ PO ₄] ⁻
1007 (m)	-	β (C-H)
961 (s)	-	ω [NH ₃] ⁺ , γ (O-H), ν_{as} [H ₂ PO ₄] ⁻
891 (m)	893 (s)	γ (O-H), ν_s [H ₂ PO ₄] ⁻ , γ (P-OH), γ (C-H)
853 (m)	836 (s)	Ring breathing
758 (w)	-	t [NH ₃] ⁺ , γ (C-H)
687 (m)	-	γ (C-H)
544 (m)	-	δ_{as} [H ₂ PO ₄] ⁻
488 (w)	-	δ_{as} [H ₂ PO ₄] ⁻
434 (w)	-	δ_{as} [H ₂ PO ₄] ⁻
-	387 (w)	δ_s [H ₂ PO ₄] ⁻
-	374 (w)	δ_s [H ₂ PO ₄] ⁻

w: Weak, s: Strong, br: Broad, m: Medium, v: Stretching, ν_s : Symmetric stretching, ν_{as} : Anti symmetric stretching, δ_s : Symmetric bending, δ_{as} : Antisymmetric bending, γ : Out-of-plane bending, β : In-plane bending, ρ : Rocking, t: Torsional, ω : Wagging

1541 cm⁻¹ in IR and at 1525 cm⁻¹ in Raman spectra, respectively. In the present study, the strong bands observed at 1138 cm⁻¹ in IR and at 1134 cm⁻¹ in Raman spectra was assigned to the rocking mode of -[NH₃]⁺ group. The -[NH₃]⁺ wagging mode was observed as a strong band at 961 cm⁻¹ in the FTIR spectrum only. The torsional mode of -[NH₃]⁺ group was also identified in the range of 760-750 cm⁻¹^{14,15}. In present case, the torsional mode vibration was observed at 758 cm⁻¹ as a medium band in the IR spectrum only. The broad band centered at 3000 cm⁻¹ in IR spectrum was attributed to the presence of extensive 3 dimensional hydrogen bonding network that exists in the crystal.

Carboxylic group vibration: The antisymmetric and symmetric stretching vibrational mode of C=O group in carboxylic acid have wavenumbers in the region 1720-1680 cm⁻¹ and 1680-1640 cm⁻¹, respectively¹³. In the present study, ν_{as} (C=O) mode occurs at 1655 cm⁻¹ in IR and at 1649 cm⁻¹ Raman spectra. Also, bands observed at 1612 cm⁻¹, 1616 cm⁻¹ in both spectra was assigned to the ν_s (C=O) mode for the title crystal. The ν (C-O) mode of carboxylic group normally occurs in the vibrational region of 1320-1210 cm⁻¹¹⁶. The title compound has wavenumbers at 1325, 1215 cm⁻¹ in IR and at 1324 cm⁻¹, 1214 cm⁻¹ in Raman spectra was attributed to ν (C-O) mode. The O-H stretch from CO-OH group was identified at 3071, 2810 cm⁻¹ in IR and at 3095, 3065, 3018, 2831 cm⁻¹ in Raman spectra, respectively for title compound. The in-plane and out-of plane bending wave numbers of O-H group

Table 3: Vibrational distribution of $[\text{PO}_4]^{3-}$ ion to $[\text{H}_2\text{PO}_4]^-$ ion

$T_d [\text{PO}_4]^{3-} (\text{cm}^{-1})$	$C_{2v} [\text{H}_2\text{PO}_4]^- (\text{cm}^{-1})$	Present study (cm^{-1})
A_1 (936)	A_1 (887)	A_1 (891)
E (420)	A_1 (357)	A_2 (338)
	A_1 (387)	A_2 (374)
F_2 (1004)	A_1 (1096)	A_1 (1067)
	B_1 (1132)	B_1 (1138)
	B_2 (964)	B_2 (961)
F_2 (573)	A_1 (529)	A_1 (545)
	B_1 (453)	B_1 (434)
	B_2 (500)	B_2 (488)

appears in the region between $1440\text{-}1395\text{ cm}^{-1}$ and $960\text{-}875\text{ cm}^{-1}$, respectively^{15,17}. In the present study, $\beta(\text{O-H})$ mode was identified as medium intensity bands at 1454 cm^{-1} , 1425 cm^{-1} in IR and at 1445 cm^{-1} in Raman spectra. Also $\gamma(\text{O-H})$ mode was attributed only at 961 cm^{-1} , 891 cm^{-1} in IR spectrum and at 893 cm^{-1} in Raman spectrum, respectively for title compound.

Para substituted benzene ring vibration: The C-H stretching mode for para substituted benzene ring was expected in the region $3115\text{-}3005\text{ cm}^{-1}$ ^{12,15}. In this case, the bands observed at 3071 cm^{-1} in IR and at $3095, 3065, 3018\text{ cm}^{-1}$ in Raman spectra was assigned to $\nu(\text{C-H})$ mode. The C-H in-plane and out-of-plane bending vibrations are seen in the range $1250\text{-}1000$ and $900\text{-}690\text{ cm}^{-1}$, respectively¹⁵. For the title compound, the $\beta(\text{C-H})$ mode was identified at $1215, 1138, 1067\text{ cm}^{-1}$ in FTIR and at $1214, 1182, 1134, 1007\text{ cm}^{-1}$ in FT-Raman spectra, respectively. The $\gamma(\text{C-H})$ mode was identified at $891, 758, 687\text{ cm}^{-1}$ in IR spectrum and at 893 cm^{-1} in Raman spectrum for the title compound. The C=C and C-C ring stretching modes occur in the region $1650\text{-}1430$ and $1400\text{-}1300\text{ cm}^{-1}$, respectively¹³. For the title compound $\nu(\text{C}=\text{C})$ mode was assigned at $1612, 1580, 1541, 1512\text{ cm}^{-1}$ in IR and $1616, 1525\text{ cm}^{-1}$ in Raman spectra. Also $\nu(\text{C-C})$ mode was observed at 1325 cm^{-1} , 1302 cm^{-1} in IR spectrum. The C-N stretching mode was identified at 1325 cm^{-1} in spectrum for this title compound. The ring breathing mode was identified at 853 cm^{-1} in IR and 836 cm^{-1} in Raman spectra for the title compound.

Dihydrogen phosphate anion vibration: The phosphate ion has T_d symmetry in the free state which has symmetric stretching $\nu_1(A_1)$, antisymmetric stretching $\nu_3(F_2)$, symmetric bending $\nu_2(E)$ and antisymmetric bending $\nu_4(F_2)$ internal vibrational modes. These wavenumbers occur at 936 cm^{-1} (ν_{sym}), 420 cm^{-1} (δ_{sym}), 1004 cm^{-1} (ν_{asym}) and 573 cm^{-1} (δ_{asym})^{18,19}. Due to the presence of two P-OH bonds, the molecular symmetry of $[\text{H}_2\text{PO}_4]^-$ ion reduces to C_{2v} symmetry. As a result, the degeneracy of the modes ν_2 , ν_3 and ν_4 was fully lifted: ν_2 splits into two components (A_1+A_2) and ν_3 and ν_4 split

into three components ($A_1+B_1+B_2$) each¹⁸. The symmetric stretching mode (A_1) normally occurs at 880 cm^{-1} and the symmetric bending mode E splits into two, appearing at 385 (A_1) and 373 (A_2) cm^{-1} . The antisymmetric stretching mode (F_2) splits into three occurring at 1090 (A_1), 1123 (B_1) and 940 (B_2) cm^{-1} . The antisymmetric bending mode (F_2) has also lost its degeneracy and was expected to occur at 525 (A_1), 510 (B_1) and 503 (B_2) cm^{-1} . All the species are both infrared and Raman active except for A_2 species, which was only Raman active¹⁹.

In the present study, the antisymmetric stretching mode of $[\text{H}_2\text{PO}_4]^-$ ion was identified at $1067(A_1)$, $1138(B_1)$, $961(B_2)\text{ cm}^{-1}$ and the symmetric stretching mode was observed in IR and Raman spectra at $891(A_1)$, $893(A_1)\text{ cm}^{-1}$, respectively. Also, the symmetric bending mode of this group was attributed at $387, 374\text{ cm}^{-1}$ in Raman spectrum only and antisymmetric bending mode was identified at $544(A_1)$, $434(B_1)$ and $488(B_2)\text{ cm}^{-1}$ in IR spectrum only. All these assignments confirm the existence of dihydrogen phosphate anion in the C_{2v} symmetry and it is clearly depicted in Table 3. The P-OH group has a strong band in the region $1040\text{-}810\text{ cm}^{-1}$ which was due to the stretching of P-OH bands²⁰. The medium bands occur at $891, 853\text{ cm}^{-1}$ in IR and at 893 cm^{-1} in Raman spectra was assigned to P-OH stretching vibration of title crystal. The in-plane and out-of-plane bending vibrations occur in the region $1350\text{-}1200$ and $950\text{-}750\text{ cm}^{-1}$, respectively^{19,20}. For the title compound these modes are identified in IR spectrum at $1215, 891\text{ cm}^{-1}$ and in Raman spectrum at $1214, 893\text{ cm}^{-1}$, respectively. The stretching vibrations of P=O generally give rise to strong band in the region $1300\text{-}1140\text{ cm}^{-1}$ for dihydrogen phosphate. The absorption bands at $1185, 1182\text{ cm}^{-1}$ in both spectra is assigned to P=O stretching mode of 4-carboxyanilinium dihydrogen phosphate crystal.

Optical analysis: 4-carboxyanilinium dihydrogen phosphate single crystal absorbance spectrum is obtained using SHIMADZU-UV1800 double beam spectrometer in the wavelength range $200\text{-}1100\text{ nm}$. The absorbance spectrum of title crystal is shown in Fig. 6. The lower cut-off wavelength was found to be at 248 nm and at 337 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 and obtained value is 3.8 eV from the Fig. 7.

SEM with EDX analysis: The morphology and elemental analysis of title compound were performed by SEM with

EDX analysis. The microphotograph of title crystal with 4 different magnifications is depicted in Fig. 8. This image reveals that the grown crystal has a smooth surface and flower like morphology. The EDX spectrum for 4-carboxyanilinium dihydrogen phosphate crystal is shown in Fig. 9. The elemental composition of title crystal is shown in Table 4. The EDX analysis reveals that C, N, O and P elements are present in the 4-carboxyanilinium dihydrogen phosphate crystal.

Antimicrobial activity study: *Staphylococcus epidermidis* (*S. epidermidis*), *Serratia marcescens* (*S. marcescens*),

Methicillin-resistant *Staphylococcus aureus* (MRSA) and Polyphosphate-accumulating organisms (PAO-1) was used to analyze the antimicrobial activity of 4-carboxyaniline parent and 4-carboxyanilinium dihydrogen phosphate complex crystals by disc diffusion method. The photographic view of bacterial screening for parent and its complex crystals are shown in Fig.10a and b, respectively. The above mentioned bacterial species were prepared at $50 \mu\text{g mL}^{-1}$ and $100 \mu\text{g L}^{-1}$ concentrations. The measured diameter zone of inhibition of these micro-organisms is shown in Table 5. Both parent and complex crystals show an effective zone of microorganism inhibition if the concentration was increased. Moreover, the

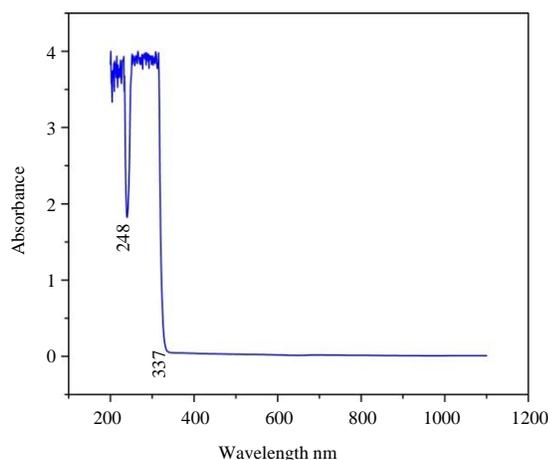


Fig. 6: Absorbance spectrum for 4-carboxyanilinium dihydrogen phosphate crystal

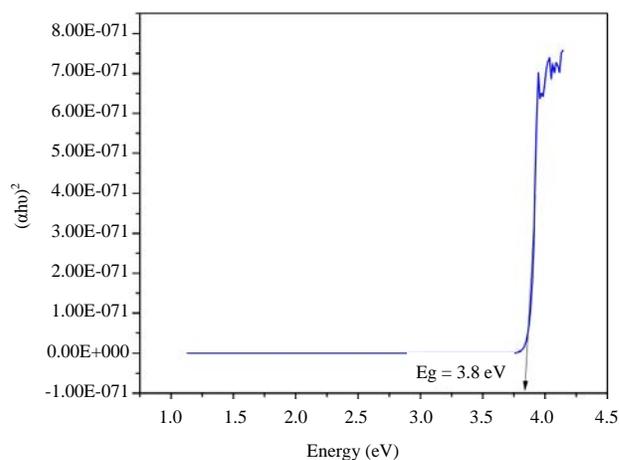


Fig. 7: Optical band gap for 4-carboxyanilinium dihydrogen phosphate crystal

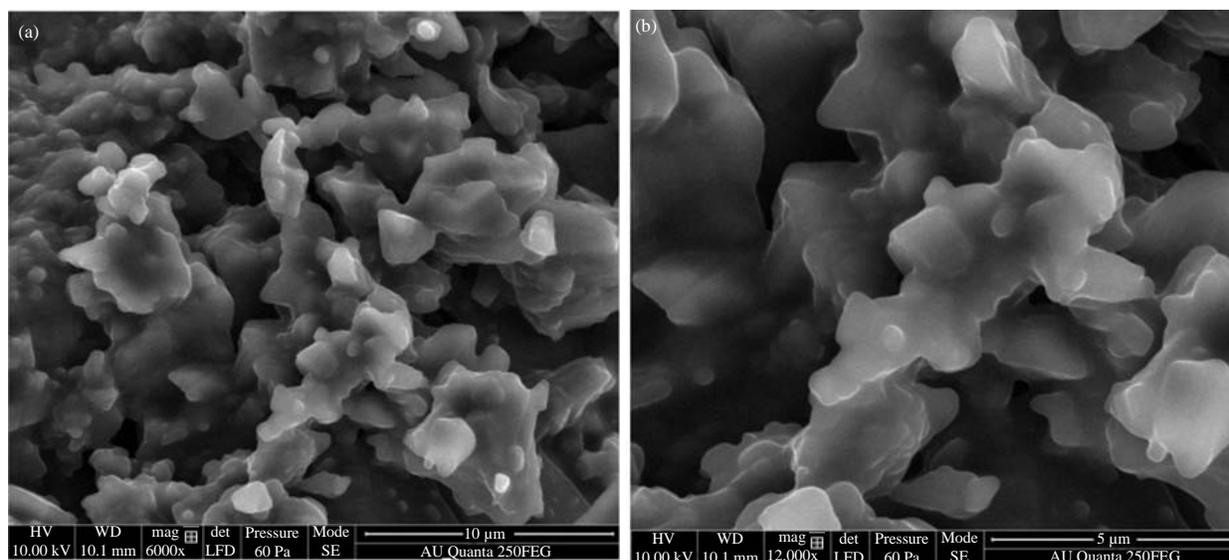


Fig. 8(a-d): Continue

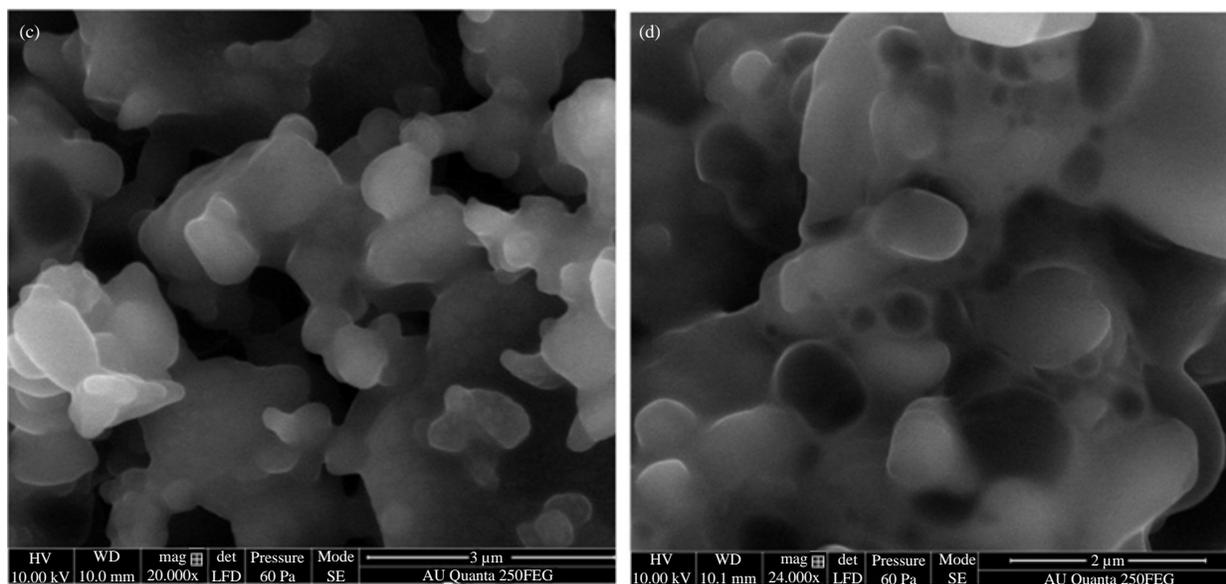


Fig.8(a-d): SEM photograph for 4-carboxyanilinium dihydrogen phosphate crystal, (a) 6000x, (b) 12,000x, (c) 20,000x and (d) 24,000x

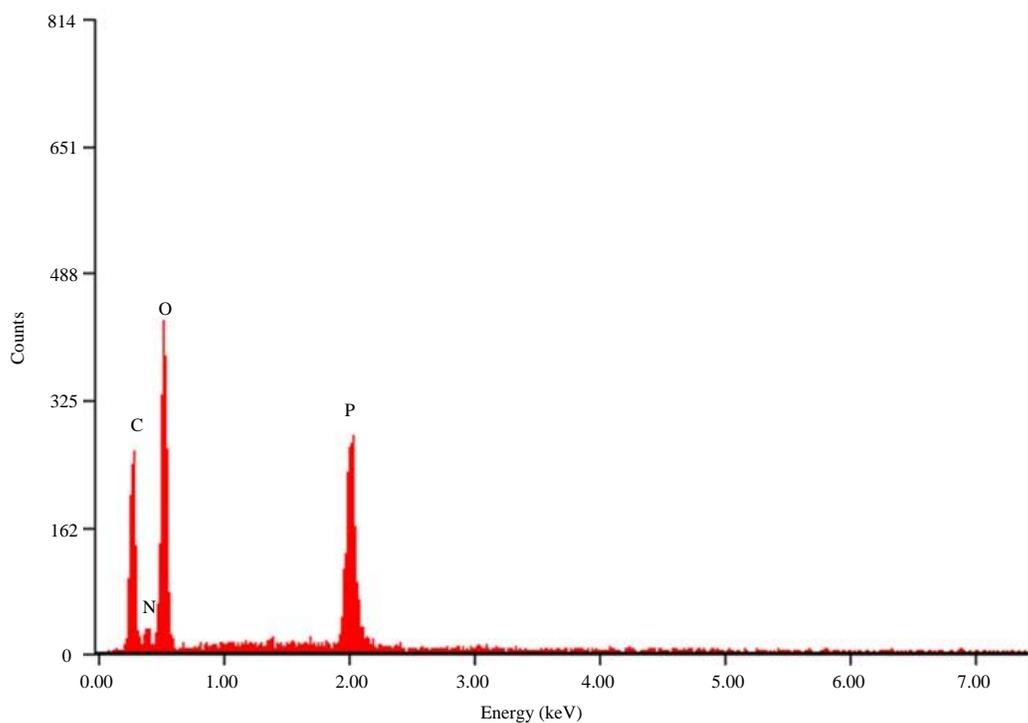


Fig. 9: EDX spectrum for 4-carboxyanilinium dihydrogen phosphate crystal

zone of inhibition for the complex crystal was increased due to the presence of phosphoric acid. Especially, it was very dominant against the *S. marcescens* bacteria. From

the Table 5, it is clear that 4-carboxyanilinium dihydrogen phosphate complex crystal was very active against all the organisms except MRSA and PAO-I. This chemically altered

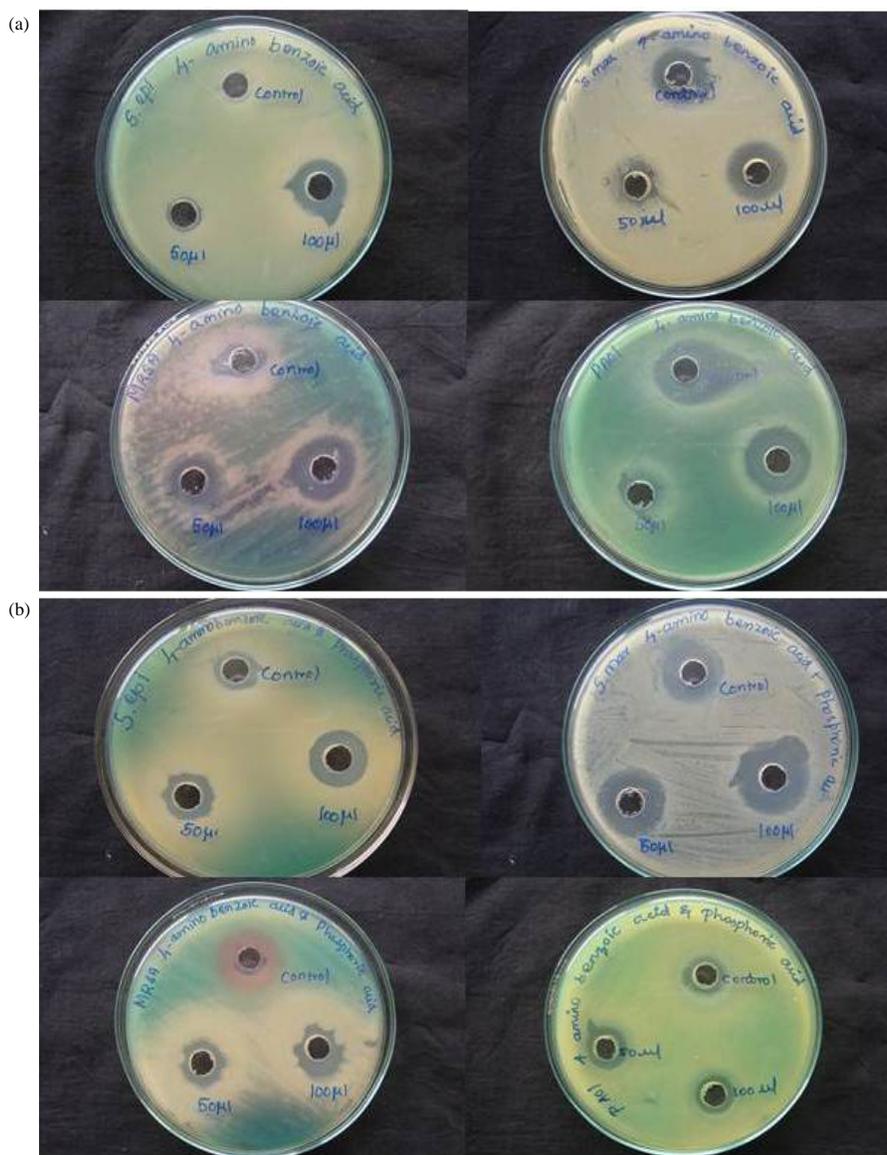


Fig. 10(a-b): Photographic view showing inhibition region of 4 different micro-organisms (a) 50 $\mu\text{g mL}^{-1}$ and 100 $\mu\text{g L}^{-1}$ concentrations against the 4-carboxyaniline parent crystal and (b) 50 $\mu\text{g mL}^{-1}$ and 100 $\mu\text{g L}^{-1}$ concentrations against the 4-carboxyanilinium dihydrogen phosphate complex crystal

Table 4: Elemental composition for 4-carboxyanilinium dihydrogen phosphate crystal

Elements	Atomic (%)
C	45.86
N	8.91
O	40.48
P	4.74

complex molecule may be used to reduce toxicity and increase solubility of drug. It was also given to the human beings in their natural form with the desirable characteristic.

Table 5: Effective values of inhibited zone for 4-carboxyaniline and 4-carboxyanilinium dihydrogen phosphate crystals

Micro-organisms	Zone of inhibition for 4-Carboxyaniline		Zone of inhibition for 4-Carboxyanilinium dihydrogen phosphate	
	50 μL (mm)	100 μL (mm)	50 μL (mm)	100 μL (mm)
S.epi	1	4	6	9
S.mar	6	10	10	13
MRSA	8	9	4	7
PAO - I	4	10	4	5

S. epi: *Staphylococcus epidermidis*, S. mar: *Serratia marcescens*, MRSA: Methicillin-resistant *Staphylococcus aureus*, PAO: 1 Polyphosphate-accumulating organisms

CONCLUSION

The 4-carboxyanilinium dihydrogen phosphate complex crystal was grown by the slow evaporation technique at room temperature in this study. It has monoclinic crystal system with the space group $P2_1/n$ as suggested by single-crystal X-ray diffraction technique. The average crystalline size of grown crystal is found to be as 54 nm and its PXRD peaks are indexed using the INDX software. Further, the presence of functional groups and elements were verified using FTIR and FT-Raman spectroscopy and energy dispersive X-ray studies. The SEM analyzes shows that the complex crystal has smooth surface and flower like morphology. The optical property of this crystal was analyzed by UV-Visible spectroscopy technique. Also, the optical band gap of title crystal is determined as 3.8 eV. The grown crystals were involved in an antibacterial activity against certain potentially threatening microbes such as *Staphylococcus epidermidis*, *Serratia marcescens*, Methicillin resistant *Staphylococcus aureus* and Polyphosphate accumulating organisms by disc diffusion method which shows that the complex crystal screened the bacteria than that of the parent crystal especially for *Staphylococcus epidermidis*, *Serratia marcescens* microorganisms.

SIGNIFICANCE STATEMENT

This study discovers the drug complex crystal that can be beneficial for people in the medicinal field. This study help the researchers to uncover the critical areas of crystal growth in organic-inorganic hybrid that many researchers were not able to explore. Thus a new theory on this complex crystal may be arrived at.

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