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Research Article

Spectral and Antimicrobial Activity Studies on 4-Carboxyanilinium Nitrate Crystal

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Abstract

Objective: The main objective of the present work was to grow 4-carboxyanilinium nitrate $C_7H_8NO_2^+ \cdot NO_3^-$ semi-organic crystal by slow evaporation method and analyzed by various techniques. The positively charged carboxyanilinium cation and nitrate anion were existing in this crystal structure. **Materials and Methods:** 4-aminobenzoic acid, nitric acid, ethanol and deionized water were used in the crystal growth process as the raw materials. The semi-organic crystal of 4-carboxyanilinium nitrate is crystallized from the aqueous ethanol solution of 4-aminobenzoic acid mixed with aqueous solution of nitric acid in 2:1 stoichiometric ratio by slow evaporation technique. **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 nitrate crystal had been recorded at room temperature. The spectra were interpreted in terms of the wavenumber assignments. The SEM analysis shows that the complex crystal has smooth surface and well defined shape morphology. The optical band gap was determined from the UV-Visible spectroscopy analysis. **Conclusion:** The unit cell parameters and space group were estimated by single crystal X-ray diffraction technique. The average crystalline size of grown crystal is found to be as 72 nm. Further, the presence of functional groups and elements were verified using FTIR and FT-Raman spectroscopy and energy dispersive X-ray studies. Also, the optical band gap of title crystal is determined as 3.90 eV. The grown crystals were involved in an antibacterial activity against certain potentially threatening microbes which shows that the complex crystal screened the bacteria than that of the parent crystal.

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

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Competing Interest: The authors have declared that no competing interest exists.

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

INTRODUCTION

The pharmaceutically important compound of p-amino benzoic acid is also known as 4-carboxyaniline¹. It is an antioxidant which can be found in most multivitamins and B complex vitamins². It is also called as vitamin B_x. However it is not really a vitamin but actually an amino acid that is part of folic acid. It can be made in the body by friendly intestinal bacteria³. In pharmaceutical field it plays an important role to relieve the pain from headaches and nervous states⁴⁻⁶. An excess ultraviolet exposure, it acts as a sun screen against the development of skin cancer and skin burn. It has two different polymorphs, the α -(fiber needles) and β -(prisms) forms^{7,8}. The 4-aminobenzoic acid derivatives show the enhanced antibacterial, antifungal, antitumor, analgesic and anti-inflammatory activities⁹. The crystal structure of 4-carboxyanilinium nitrate was already reported by Athimoolam and Natarajan¹⁰, the vibrational and antimicrobial activity studies of 4-carboxyanilinium perchlorate monohydrate were also reported recently by Muthuselvi *et al.*¹¹ and spectroscopy study of 4-carboxyanilinium chlorate, bromate were reported recently by Susindran *et al.*¹². But, there is no report on the spectroscopy and antimicrobial studies of 4-carboxyanilinium nitrate semi-organic crystal. So objective of present study to made an attempt on the growth of 4-carboxyanilinium nitrate semi-organic crystal by slow evaporation method. The grown crystal was characterized by single crystal XRD, powder XRD, FTIR, FT-Raman, UV-Visible spectroscopy, SEM with EDX and antimicrobial activity studies.

MATERIALS AND METHODS

The raw materials used for this crystal growth were 4-aminobenzoic acid, nitric acid, ethanol and deionized water and they were purchased from Sigma Aldrich Company, India. The semi-organic crystal of 4-carboxyanilinium nitrate was crystallized from the aqueous ethanol solution of 4-aminobenzoic acid mixed with aqueous solution of nitric acid in 2:1 stoichiometric ratio by slow evaporation technique. This solution was stirred well for 1 h and after filtering process it was poured into the petri dish. After a period of 2 weeks, bulk crystal of title compound was harvested and is shown in Fig. 1. The selected good quality crystal of 4-carboxyanilinium nitrate was used to carry out the single crystal X-ray diffraction using Bruker SMART APEX CCD diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The unit cell dimension and space group of the title compound were determined and compared with the already reported values¹⁰. The XPERT-PRO X-ray diffractometer with Cu K α

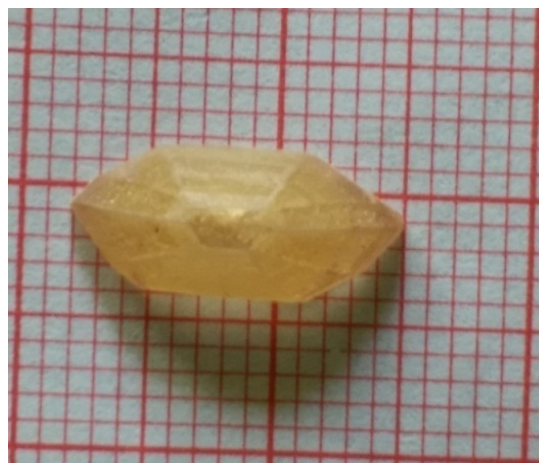


Fig. 1: Grown crystal of 4-carboxyanilinium nitrate

($\lambda = 1.54060 \text{ \AA}$) radiation was used to record the powder diffraction pattern. The FTIR vibrational spectrum was recorded by using SHIMADZU FTIR spectrometer in the range $4000-400 \text{ cm}^{-1}$, the FT-Raman spectrum was also recorded by using the BRUKER, RFS 27 Raman spectrometer in the wavenumber range $4000-400 \text{ cm}^{-1}$. The optical absorbance spectrum of 4-carboxyanilinium nitrate semi-organic crystal has been recorded with SHIMADZU-UV1800 double beam spectrometer in the wavelength range $200-1100 \text{ nm}$ in steps of 1 nm . The surface morphology and elemental analysis has been carried out by CARLZEISS EVO18 scanning electron microscope. Using the disc diffusion method, the antimicrobial activity of parent and its complex crystals were tested against 5 different kinds of microorganisms.

RESULTS AND DISCUSSION

Single crystal XRD: The single crystal X-ray diffraction was done using the SMARTAPEX CCD area-detector diffractometer for the title crystal. It gives the unit cell parameter and space group of 4-carboxyanilinium perchlorate crystal. Initially, these were checked with the Cambridge Structural Database (CSD) for confirmation. The report shows that the grown crystal was exactly matched with already reported values¹⁰. The crystallographic data of grown crystal of 4-carboxyanilinium nitrate is shown in Table 1 and was compared with already reported values¹⁰. The molecular structure of 4-carboxyanilinium nitrate crystal is depicted in Fig. 2. This study reveals that the grown crystal was a complex one, since the proton transfer has taken place from nitric acid to 4-carboxyaniline amino NH_2 group and then it becomes as 4-carboxyaniline cation and nitrate anion. Also this study

confirms the grown crystal crystallizes in the monoclinic system with space group P2₁/c.

Powder XRD analysis: The powder X-ray diffraction pattern of 4-carboxyanilinium nitrate crystal was recorded using

Table 1: Crystallographic data of 4-carboxyanilinium nitrate crystal

Parameters	Present study	Already reported ¹⁰
Compound name	4-Carboxyanilinium nitrate	4-Carboxyanilinium nitrate
Empirical formula	C ₇ H ₈ NO ₂₊ ⁺ ·NO ₃ ⁻	C ₇ H ₈ NO ₂₊ ⁺ ·NO ₃ ⁻
Molecular formula weight	200.15	200.15
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /c	P2 ₁ /c
Unit cell dimensions	a = 8.83 Å b = 15.15 Å c = 6.75 Å α = 90° β = 90.875° γ = 90°	a = 8.82 Å b = 15.05 Å c = 6.70 Å α = 90° β = 90.933° γ = 90°
Volume	889.16 Å ³	888.14 Å ³

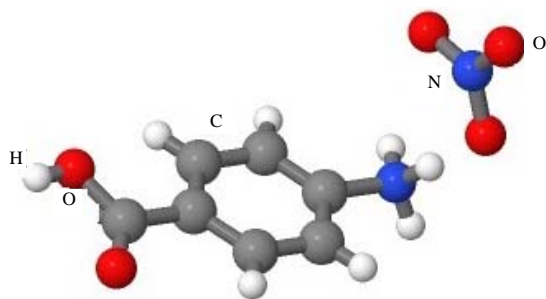


Fig. 2: Molecular structure of 4-carboxyanilinium nitrate

XPRT-PRO X-ray diffractometer with Cu Kα (λ = 1.54060 Å) radiation from 10-80° at 10°/sec scan step time. The experimentally recorded XRD pattern of the title crystal is shown in Fig. 3 and the peaks are indexed using indx software. The sharp intense peaks emerged out from the XRD pattern. The sharp intensity peaks found in PXRD pattern shows good crystalline nature and purity of the grown crystal. The average crystalline size of 4-carboxyanilinium nitrate crystal was determined by using the Debye-Scherrer equation, 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 Kα = 1.54060Å)

θ = Diffraction angle

β = Full width at half maximum intensity

The dislocation density can be calculated from:

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

Where:

δ = Dislocation density

D = Crystallite size

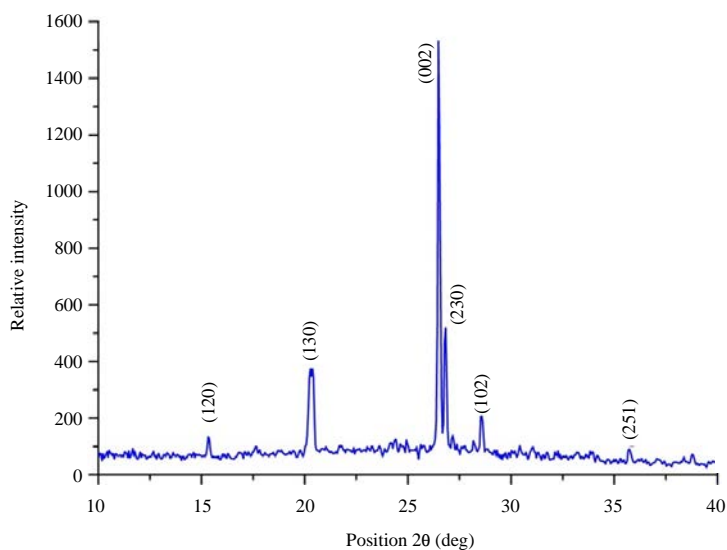


Fig. 3: Diffraction patterns for 4-carboxyanilinium nitrate crystal

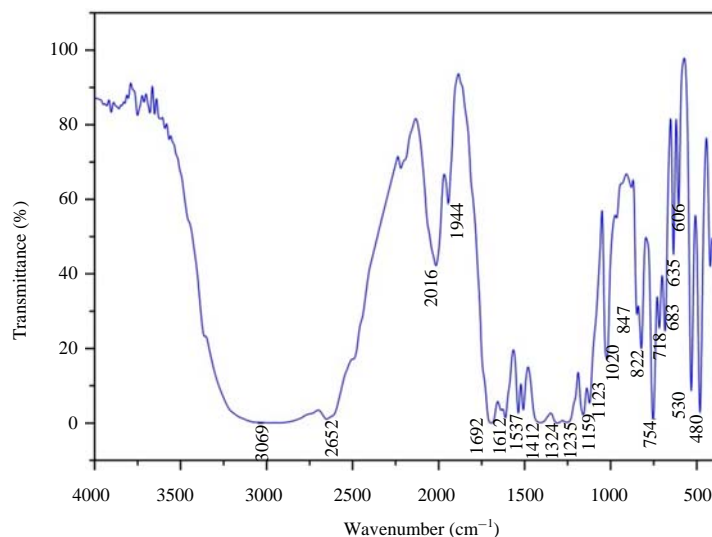


Fig. 4: FTIR spectrum for 4-carboxyanilinium nitrate crystal

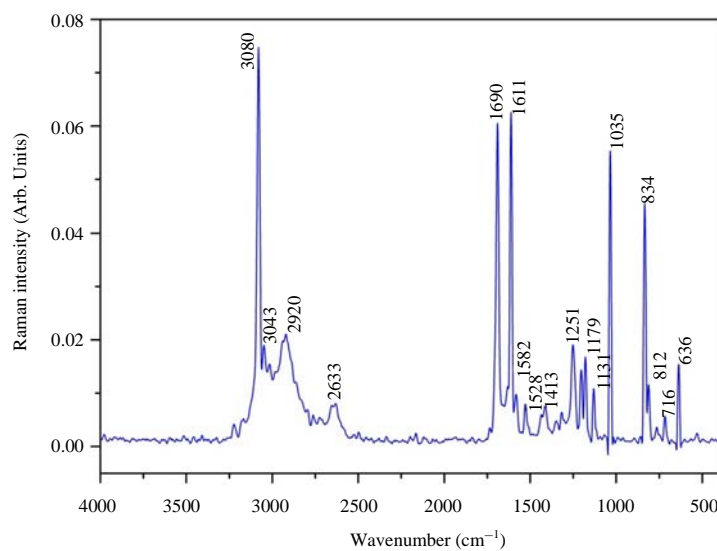


Fig. 5: FT-Raman spectrum for 4-carboxyanilinium nitrate crystal

For the 4-carboxyanilinium nitrate crystal, the average crystalline size is found to be as 72 nm. The dislocation density of this crystal is determined as $1.88 \times 10^{14} \text{ m}^{-2}$.

Vibrational analysis: The 4-carboxyanilinium nitrate has $-\text{[NH}_3\text{]}^+$, $-\text{COOH}$, para substituted benzene ring and NO_3^- functional groups. The intensity and position of these groups were expected to change due to the presence of hydrogen bonds. The FTIR and FT-Raman spectra of title compound are shown in Fig. 4 and 5, respectively. The detailed wavenumber assignment for this compound is shown in Table 2.

Vibration of $-\text{[NH}_3\text{]}^+$ cation: The antisymmetric and symmetric stretching mode of $-\text{[NH}_3\text{]}^+$ anilinium group has the strong absorption band between 3200 and 2800 cm^{-1} ¹³. Also, the $-\text{[NH}_3\text{]}^+$ antisymmetric and symmetric deformation wavenumbers were normally expected to fall in the region 1625 - 1550 and 1550 - 1505 cm^{-1} , respectively^{13,14}. For the title crystal, the antisymmetric stretching mode was attributed due to strong broad band at 3069 cm^{-1} in IR spectrum and strong band at 3080 cm^{-1} in Raman spectrum, respectively in the present study. Also, the bands at 3049 , 2920 cm^{-1} in Raman spectrum were assigned to the symmetric stretching mode of

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

FTIR ($\tilde{\nu}$ cm ⁻¹)	FT-Raman ($\tilde{\nu}$ cm ⁻¹)	Assignment
3069 (s, br)	3080 (s)	ν_{as} [NH ₃] ⁺ , ν (C-H)
-	3049 (w)	ν_s [NH ₃] ⁺ , ν (O-H), ν (C-H)
-	2920 (w)	ν_s [NH ₃] ⁺ , ν (O-H)
1692 (s)	1690 (s)	ν_{as} (C=O)
1636 (s)	-	ν (C=C), ν_s (C=O)
1612 (m)	1611 (s)	ν (C=C), δ_{as} [NH ₃] ⁺
-	1582 (m)	ν (C=C)
1537 (s)	1528 (m)	δ_s [NH ₃] ⁺
1506 (m)	-	ν (C=C)
1412 (s)	1413 (w)	β (O-H)
-	1343 (w)	ν (C-C), ν_{as} (NO ₃) ⁻
1324 (s)	1324 (m)	ν (C-C), ν (C-O), ν (C-N), β (O-H)
1235 (w)	1251 (m)	ν (C-O)
1159 (s)	1179 (w)	β (C-H)
1123 (m)	1131 (m)	ρ [NH ₃] ⁺ , β (O-H), β (C-H)
1020 (m)	1035 (s)	β (C-H), ν_s (NO ₃) ⁻ , β (C-H)
964 (w)	-	ω [NH ₃] ⁺
932 (w)	-	γ (O-H)
847 (w)	834 (s)	Ring breathing mode, γ (NO ₃) ⁻
822 (w)	812 (w)	γ (NO ₃) ⁻
754 (m)	-	γ (C-H), γ (NO ₃) ⁻
718 (w)	716 (w)	γ (C-H), β (NO ₃) ⁻
530 (m)	-	t [NH ₃] ⁺
480 (m)	-	t [NH ₃] ⁺

w: Weak, s: Strong, m: Medium, ν : 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: Twisting, ω : Wagging

-[NH₃]⁺ group. The corresponding IR counterpart merges in the strong broad band centered around 3000 cm⁻¹. The wavenumbers were assigned at 1612, 1611 cm⁻¹ in both spectra for δ_{as} -[NH₃]⁺ mode and at 1537 (IR), 1528 cm⁻¹ (Raman) for δ_s -[NH₃]⁺ mode in the present study. In the compound under study, rocking of -[NH₃]⁺ group was observed at 1123 cm⁻¹ as a medium band in the infrared spectrum and as a strong band at 1131 cm⁻¹ in Raman spectrum. The -[NH₃]⁺ wagging mode was observed as a weak peak at 964 cm⁻¹ in the FTIR spectrum only. The twisting vibrations of -[NH₃]⁺ were observed as weak bands at 530 and 480 cm⁻¹ in IR spectrum. The corresponding vibrations were observed Raman spectrum and their assignments were in good agreement with the earlier reports¹⁴⁻¹⁶. The observed stretching and bending modes of -[NH₃]⁺ group appear at slightly lower and higher wave number side, respectively due to the effect of coordination and hydrogen bonding than those expected for free ion. The broad band centered at 3000 cm⁻¹ in IR spectrum was attributed to the presence of extensive three dimensional hydrogen bonding (N-H...O) network that exists in the crystal.

Vibrations of para substituted benzene ring: The para substituted benzene ring C-H stretching mode was expected in the region 3115-3005 cm⁻¹^{17,18}. In the present study, the bands observed at 3069 cm⁻¹ and at 3080, 3049 cm⁻¹ in IR and

Raman spectra, respectively was 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 and 900-690 cm⁻¹, respectively¹⁷. For the title compound, β (C-H) mode was attributed at 1159, 1123, 1020 cm⁻¹ in FTIR and 1179, 1035 cm⁻¹ in FT-Raman spectra, respectively. The γ (C-H) mode was observed at 754, 718 cm⁻¹ in IR and at 716 cm⁻¹ in Raman spectra, respectively for the title compound. The C=C and C-C ring stretching modes were observed between the region 1650-1430 and 1400-1300 cm⁻¹, respectively¹⁹. The ν (C=C) mode was assigned at 1636, 1612, 1506 cm⁻¹ in IR and 1611, 1582, 1528 cm⁻¹ in Raman spectra. Also ν (C-C) mode was observed at 1324 cm⁻¹ in IR spectrum and at 1343, 1324 cm⁻¹ in Raman spectra for the title compound. The C-N stretching mode was identified at 1324 cm⁻¹ in both spectra for this title compound. The ring breathing mode was identified at 847 cm⁻¹ in IR and 834 cm⁻¹ in Raman spectra for the title compound.

Vibrations of carboxylic group: The C=O antisymmetric and symmetric stretching mode of carboxylic group have wavenumbers in the region 1720-1680 and 1680-1640 cm⁻¹, respectively²⁰. In the present study, the bands occurs at 1692, 1690 cm⁻¹ in IR and Raman spectra was assigned to ν_{as} (C=O) mode. Also, bands at 1636 cm⁻¹ in IR spectrum was 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⁻¹²¹. The title compound has the wavenumbers at 1324, 1235 cm⁻¹ in IR and at 1324, 1251 cm⁻¹ in Raman spectra was attributed to ν (C-O) mode. The O-H stretch from CO-OH group was identified at 3065-2826 cm⁻¹^{21,22}. It was attributed at 3049, 2920 cm⁻¹ in Raman spectrum for title compound. The in-plane and out-of-plane bending wavenumbers of O-H group appears in the region between 1440-1395 and 960-875 cm⁻¹, respectively^{21,22}. In the present study, β (O-H) mode was observed at 1412, 1324 cm⁻¹ in IR and at 1413, 1324 cm⁻¹ in Raman spectra. Also γ (O-H) mode was attributed only at 932 cm⁻¹ in IR spectrum of title compound.

Vibrations of NO₃⁻ anion: The planar NO₃⁻ (D_{3h}) ion has 4 fundamental modes, i.e., antisymmetric stretching at approximately 1330 cm⁻¹ (doubly degenerated, both IR and Raman-active), symmetric stretching at 1040 cm⁻¹ (Raman-active), out-of-plane bending at 800 cm⁻¹ (IR-active) and in-plane bending at 730 cm⁻¹ (doubly degenerated, both IR and Raman-active)^{19,23}. For anilinium nitrate compound, the antisymmetric stretching mode of NO₃⁻ group are observed at 1340, 1344 cm⁻¹ in IR and Raman spectra, respectively. In

the present study, this mode has been found at 1343 cm^{-1} in Raman spectrum only. The symmetric stretching mode of NO_3^- group was observed as the two infrared bands of strong and medium intensity at 1038 and 1031 cm^{-1} for anilinium nitrate crystal²³. For the title compound, this mode was attributed at 1020 and 1035 cm^{-1} in IR and Raman spectra, respectively. Also, out of plane bending mode of NO_3^- group for anilinium nitrate crystal²³ were observed at 835 and 822 cm^{-1} in the IR spectrum. In the present case, this mode was identified at $847, 822\text{ cm}^{-1}$ in the IR spectrum for the 4-carboxyanilinium nitrate crystal. The splitting of this mode into a doublet may be ascribed to a lowering of symmetry of NO_3^- the ion from D_{3h} to C_{2v} or C_s . Also, the in-plane bending mode was assigned $718, 716\text{ cm}^{-1}$ in both spectra for the title crystal.

Optical analysis: The absorbance spectrum of 4-carboxyanilinium nitrate crystal was obtained by using SHIMADZU-UV1800 double beam spectrometer in the wavelength range $200\text{--}1100\text{ nm}$. The experimentally recorded absorbance spectrum is shown in Fig. 6. The lower cut-off wavelength was found to be at 330 nm for 4-carboxyanilinium nitrate crystal. It has 100% transmittance between longer UV region to shorter IR region including the entire visible spectrum which tells the usefulness of this material in optical applications. The energy gap E_g was 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 extrapolating the linear portion of $(\alpha h\nu)^2$ to the photon energy axis. This gives energy gap value of 4-carboxyanilinium nitrate crystal. It is found at 3.90 eV from the Fig. 7.

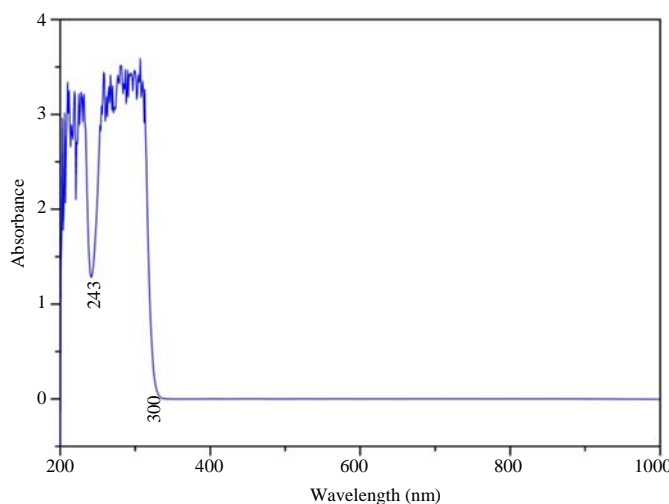


Fig. 6: Absorbance spectrum for 4-carboxyanilinium nitrate crystal

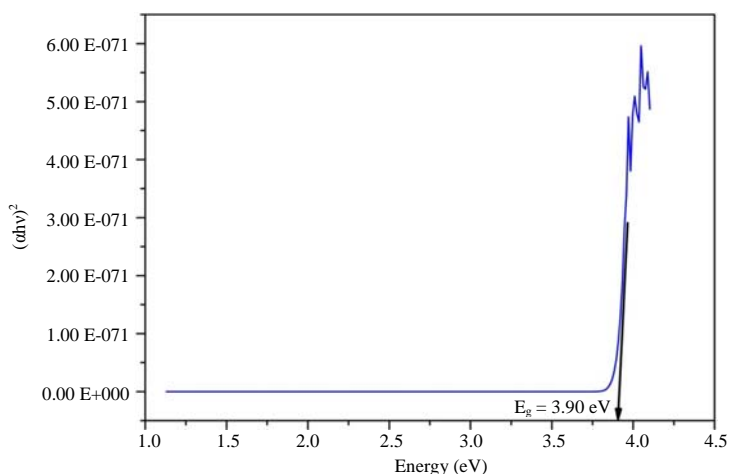


Fig. 7: Optical band gap for 4-carboxyanilinium nitrate crystal

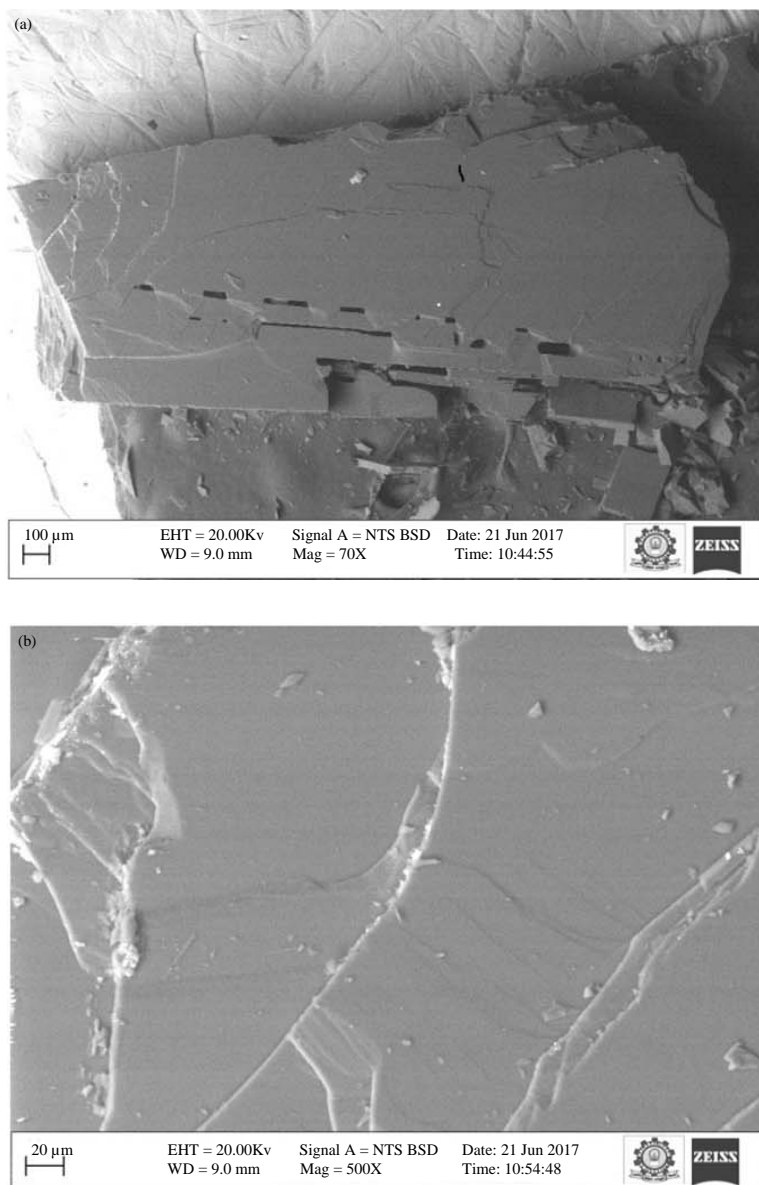


Fig. 8(a-b): SEM photograph for 4-carboxyanilinium nitrate crystal, (a) 70x and (b) 500x

SEM with EDX analysis: The morphology and elemental analysis were performed by SEM with EDX analysis. The microphotograph of title crystal is depicted in Fig. 8. This image reveals that the grown crystal has a smooth surface and well defined shape. The EDX spectrum of title crystal is shown in Fig. 9. The composition of element present in crystal is shown in Table 3. The elemental distribution analysis reveals the presence of C, N and O in the title crystal.

Antimicrobial activity study: The 4-carboxyaniline and 4-carboxyanilinium nitrate crystals were tested against *Staphylococcus epidermidis* (*S. epi*), *Serratia marcescens*

Table 3: Elemental composition for 4-carboxyanilinium nitrate crystal

4-carboxyanilinium nitrate		
Elements	Atomic (%)	Weight (%)
C	17.85	5.24
N	37.21	12.21
O	44.19	16.22

(*S. mar*), Methicillin-resistant *Staphylococcus aureus* (MRSA), *Chromobacterium violaceum* (*C. Vio*) and Polyphosphate-accumulating organisms (PAO-1) to analyze the antimicrobial activity by disc diffusion method. The photographic view of bacterial screening after inhibition by

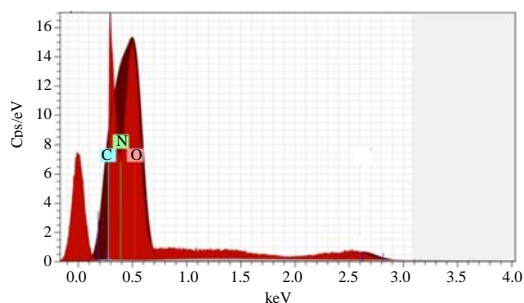


Fig. 9: EDX spectrum for 4-carboxyanilinium nitrate crystal

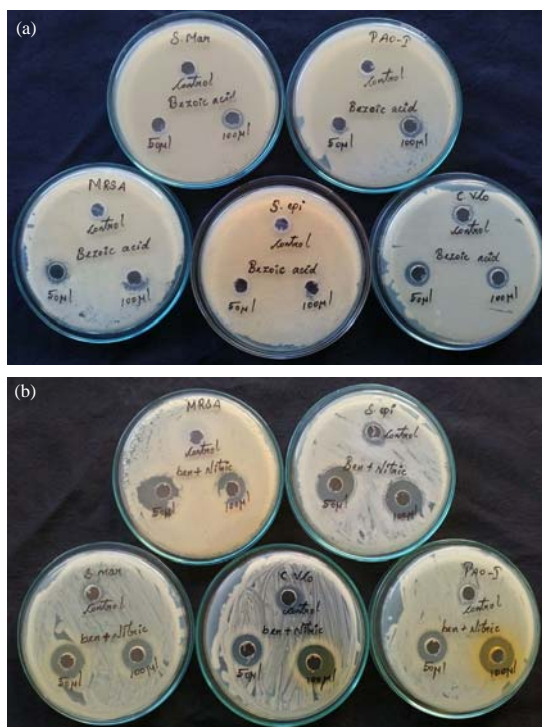


Fig. 10(a-b): Photographic view showing inhibition region of 5 different microorganisms (a) At $50 \mu\text{g mL}^{-1}$ and $100 \mu\text{g L}^{-1}$ concentrations against 4-carboxyaniline parent crystal, (b) At $50 \mu\text{g mL}^{-1}$ and $100 \mu\text{g L}^{-1}$ concentrations against 4-carboxyanilinium nitrate complex crystal

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 microorganisms is shown in Table 4. Parent and complex crystals both show an effective zone of microorganism inhibition and they do not have any impact on the change of concentration. Moreover, the zone of inhibition for

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

Microorganisms	Zone of inhibition for 4-carboxyaniline		Zone of inhibition for 4-carboxyanilinium nitrate	
	50 μL (mm)	100 μL (mm)	50 μL (mm)	100 μL (mm)
S.epi	NIL	NIL	6	7
S.mar	NIL	3	6	6
MRSA	3	3	10	6
C.vio	4	3	5	6
PAO - I	NIL	3	5	6

Staphylococcus epidermidis (S. epi), *Serratia marcescens* (S. mar), Methicillin-resistant *Staphylococcus aureus* (MRSA), *Chromobacterium violaceum* (C. Vio) and Polyphosphate-accumulating organisms (PAO-1)

the complex crystal was increased due to the doping of nitric acid. Especially, it was very dominant against the MRSA bacteria. From the Table 4, it was clear that 4-carboxyanilinium nitrate complex was moderately active against all the organisms.

CONCLUSION

A semi-organic crystal of 4-carboxyanilinium nitrate was grown by the slow evaporation technique at room temperature. The unit cell parameters and space group were estimated by single-crystal X-ray diffraction technique. This study reveals that the title compound crystallized in the monoclinic crystal system with the space group $P2_1/c$. The average crystalline size of grown crystal is found to be as 72 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 well defined shape 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 3.90 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*, *Chromobacterium violaceum* and Polyphosphate-accumulating organisms by disc diffusion method which shows that the complex crystal screened the bacteria than that of the parent crystal.

SIGNIFICANCE STATEMENTS

This study discovers the new drug complex crystal that can be beneficial for human beings in pharmaceutical field.

This study help the researchers to uncover the critical areas of crystal growth of drug complexes that many researchers were not able to explore. Thus a new drug complex crystal with other combinations may be arrived at in the medicinal field to improve the solubility of drug.

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