

FTIR and Raman Vibrational Investigations on the Complex of Pyridine with Tartaric Acid

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Abstract: Amino acids are the building blocks of proteins and an important class of molecules, which are found to exhibit characteristic aggregation patterns in their crystal structures. Especially, the head-to-tail hydrogen bonding patterns that have been observed in the crystal structures of amino acids are of intrinsic interest pertaining to characteristic aggregation patterns. Carboxylic acids are simple organic molecules that are believed to have existed in the prebiotic earth and some of them are key intermediates in the biosynthesis of organic acids. Pyridine is used as a precursor to agrochemicals and pharmaceuticals and is also an important solvent and reagent. Tartaric acid is used as an antioxidant and its derivatives have a plethora of uses in the field of pharmaceuticals. For example, tartaric acid has been used in the production of effervescent salts, in combination with citric acid, in order to improve the taste of oral medications. In the present investigation, the complete vibrational analysis of the title compound is carried out in detail using FTIR and FT Raman measurements.

Keywords: Amino acids, Carboxylic acids, Pyridine, Tartaric acid, Infrared Spectroscopy, Raman Spectroscopy.

I. Introduction

Crystallographic Study of Pyridinium Tartarate revealed that these crystals belong to the P_{212121} space group of orthorhombic geometry. In the present case, the carboxylic group of tartaric acid accepts hydrogen from the Pyridine. Hence the structure consists of Pyridine cation and Tartaric acid anion. The crystal structure has various functional groups such as NH^+ , C-H, C=O, C-N=C, COO(H), C-N, OH, COO⁻. The modes with low wave numbers are related to external, vibrational and rotational modes and contain compressed torsion of C-C structure, C-C-C bending and deformation vibration of various groups. The waves with higher wave numbers are due to NH^+ and CH stretching frequencies. The bands below 200 cm^{-1} are due to lattice vibrations. Infrared (IR) and Raman spectral studies are useful for elucidating the structural features and molecular functioning of molecules. The vibrational spectral analysis of some amino acids combined with organic acids has already been carried out [Ramasamy et al., 2002; Rajkumar et al., 2000][1,2]. As a continuation of the spectroscopic studies on amino acid-organic acid complexes, the present study investigate in detail the complete vibrational spectra of Pyridinium Tartarate with the help of the infrared and Raman data.

II. Experimental

Pyridinium Tartarate crystals were crystallized by slow evaporation technique at room temperature from an aqueous solution containing Pyridine and Tartaric acid in the stoichiometric ratio of 1:1. Colorless, thin, transparent crystals of Pyridinium Tartarate were obtained after about 2 weeks and were collected. A Bruker IFS66V FT (IR) spectrometer was used to record the IR spectra at CECRI, Karaikudi. A Bruker RFS27 Spectrometer was used to record the FT-RAMAN Spectral measurements at SAIF, IIT, Madras.

III. Results and Discussion

3.1 Crystal Structure Analysis

An X-ray crystal structure elucidation of Pyridine Tartaric($C_5H_6N^+$)($C_4H_5O_6^-$), revealed that these crystal belong to the orthorhombic system with P_{212121} space group and the cell parameters are $a=5.0390\text{ \AA}$, $b=13.220\text{ \AA}$, $c=15.318\text{ \AA}$ and $V=1020.5(\text{\AA}^3)$, $Z=4$, $D_x=1.492\text{ Mgm}^{-3}$. Based on the comparison of crystallographic data of the parents Pyridine and Tartaric acid with that of the titled crystal, new complex formation is confirmed.[Suresh et al.,2006[5-8]]

The titled compound, Pyridine molecule exists in the cationic form, with positively charged amine group. Tartaric acid molecules exist in the anionic form. The structural formula of the title compound is shown in Fig.1

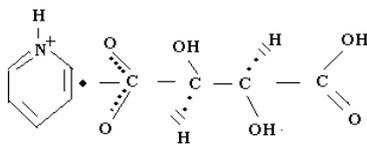


Fig 1: Structural formula of Pyridinium Tartarate

The observed FTIR and Raman spectra are presented in Fig.2 and Fig.3 respectively.

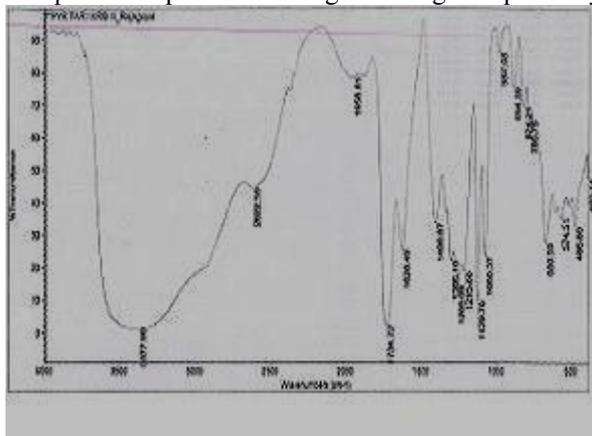


Fig 2: IR Spectrum of Pyridinium Tartarate

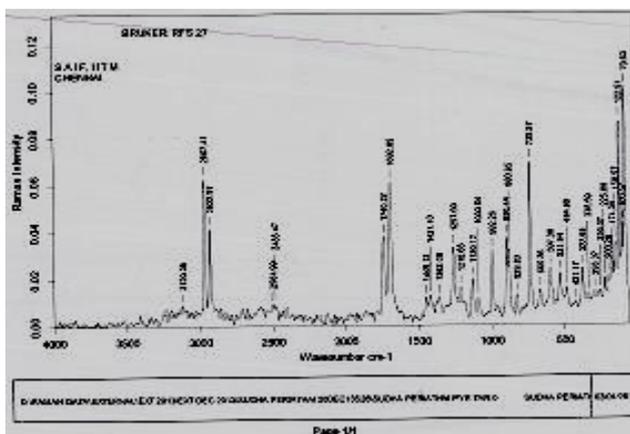


Fig 3: Raman Spectrum of Pyridinium Tartarate

From the observed vibrational bands of IR and Raman spectra, the tentative assignments are made [Table 1]. In the title compound, a large degree of hydrogen bonding is expected to modify the spectra from that of the parent molecules.

Characteristic frequency cm^{-1}	Observed Frequency cm^{-1}		Assignments
	IR spectrum	Raman spectrum	
Vibrations of C-H stretching			
3400-3070	3000-3700	3120	NH, CH Asym.stretching
3000-2900	2922	2967	CH stretching
	-	2932	CH stretching
2897-2865	-	-	
2820-2710	-	-	
Vibrations of C=O stretching			
1725-1700	1735	1740	C=N, C=O stretching
Vibrations of C-O-C			
1200-1180	1215	1210	Asym C-O-C Stretching
1180-1130	1129	1130	Sym. C-O-C stretching
Vibrations of C-H bending			
840-790	824	1440, 828	C-C Str, C-H Out of plane
730-665	680	666	C-C Out of plane bending
682-610	-	-	C-H bending

Vibrations of O-H stretching			
3300-2500	2622	3120	O-H stretching
	-	2501	O-H stretching
Vibrations of C-H deformation			
1475-1450	-	1449	CH Asym. stretching
1440-1405	1408	1421	CH bending
1375-1350	-	1362	CH bending
1300-1240	1265	1257	CH in plane bending
Vibrations of NH ⁺ groups			
3130-3030	3100-3000	3120	NH Stretching
1660-1600	1628	-	NH Asym. bending
Skeletal and Lattice Vibrations			
1132-885	1129	1130	C-C Skeletal
	1080	1090	C-C Skeletal
	987	992	C-C Skeletal
	894	896	C-C Skeletal
Below 200	-	171	Lattice Vibrations
	-	158	Lattice Vibrations
	-	122	Lattice Vibrations
	-	100	Lattice Vibrations
	-	79	Lattice Vibrations

Table1. Tentative band assignments

3.2 Vibrational Analysis

The crystal structure consists of various functional groups such as NH⁺, C-H, C=O, C-O(H), COO⁻ and skeletal vibrations such as C-C, C-C-N, C-N.

3.2.1 NH⁺ vibration

The -NH⁺ asymmetric and symmetric modes occur between 3200 cm⁻¹ and 2800 cm⁻¹. The asymmetric -NH⁺ deformation modes appear at 1625 cm⁻¹ -1560 cm⁻¹ and 1550 cm⁻¹ -1505 cm⁻¹, respectively [Colthup et al., 1990][9]. The stretching wave numbers of the crystalline -NH⁺ group are lower than those of free -NH group. This is because of the effect of coordination. Upon coordination, the N-H bond is weakened and the stretching wave numbers are lowered. The stronger the C-N bond the weaker is the N-H bond and lower are the -NH⁺ group stretching vibrations. The C-N bond strength can be measured using the -NH⁺ stretching wave numbers [Nakamoto, 1986][10]. The effects of hydrogen bonding and coordination shift the -NH⁺ deformation and rocking modes to higher wave numbers. Among these the -NH⁺ rocking mode is more sensitive and the deformation mode is less sensitive to these effects. The observation of strong band at 3120 cm⁻¹ in Raman assigned to the stretching vibrations of -NH⁺ group. The -NH⁺ asymmetric bending mode of vibration occur at 1628 cm⁻¹ in IR. These modes are lowered by about 200 cm⁻¹ than the expected free ion values. The degenerate -NH⁺ asymmetric deformation mode appears at 1628 cm⁻¹ in IR and at 1692 cm⁻¹ in Raman.

3.2.2 C-H group vibrations

The C-H stretching wave numbers appear between 3300 cm⁻¹ -2800 cm⁻¹. For the compound under study, the CH stretching vibration appears as a medium intensity band around 2932 cm⁻¹ in the Raman. The peak at 2967 cm⁻¹ in Raman spectrum assigned to CH stretching mode. The peak at 1265 cm⁻¹ in IR and 1257 cm⁻¹ in Raman are assigned to C-H deformation mode. The C-H coupled vibrations of CH₂ groups are of different wave number than C-H stretching vibration. The CH bending deformation mode is located at 1408 cm⁻¹ in IR and 1421 cm⁻¹ in Raman. The wagging mode of CH group appears at 1362 cm⁻¹ in Raman. The in - phase CH rock vibration is observed at 824 cm⁻¹ in IR and 828 cm⁻¹ in Raman.

The vibrations of C-C out of plane bending mode appear at 680 cm⁻¹ in IR and 666 cm⁻¹ in Raman. This causes coupling between adjacent CH groups and as a result the wagging (1380 cm⁻¹-1170 cm⁻¹) twisting (1295 cm⁻¹ - 1063 cm⁻¹), and rocking (1175 cm⁻¹-720 cm⁻¹) wave numbers are spread over a range [Colthup et al., 1990][9]. The presence of a larger number of vibration bands for the CH group confirms the fact that the tartaric acid molecule has a long chain of CH groups.

3.2.3 C-N, C-C-N vibrations

The absorption bands arising from C-N stretching vibration observed in the wave number region 850-1150 [colthup et al., 1990][9]. In the present investigated crystal the strong band at 1129 cm⁻¹ in IR and Raman band at 992 cm⁻¹ & 1130 cm⁻¹ can be assigned to C-N stretching vibration. The intensity band at 1080 cm⁻¹ in IR and 1090 cm⁻¹ in Raman assigned to the asymmetric stretching vibration of C-C-N.

3.2.4 C=O, C-O-C vibration

Usually carboxyl group show its characteristic bands. The carbonyl C=O stretching vibration absorbs strongly in the region (1755 cm^{-1} - 1700 cm^{-1}) [Liu et al., 1998][3]. The band at 1734 cm^{-1} in IR attributed to this group. Pyridinium tartarate molecule has a deprotonated carboxylic group. It is well known that on ionized carboxylic group[COO^{-}] has characteristics wave number [Hubert et al.1991,Bellamy,1975][4,11] in the regions 1680 cm^{-1} - 1540 cm^{-1} (strong asymmetric stretching) 1410 cm^{-1} (Weak symmetric stretching) and 660 cm^{-1} (symmetric deformation). In the compound under study, the carboxylic group is not free, since one of the Oxygen in the ionized carboxylic group is Hydrogen bonded to the Nitrogen atom of the amino group. This weakens the O-C-O bonds and lowers the wave number of the corresponding stretching mode. The strong and broad peak at 1630 cm^{-1} in IR and the corresponding low intensity peak at 1692 cm^{-1} in the Raman spectrum have been assigned to the carboxylic asymmetric stretching mode, with are about 50 cm^{-1} lower than the expected range owing to hydrogen bonding.

The symmetric modes C-O-C are expected to show its character band at 1180 cm^{-1} - 1130 cm^{-1} . The bands at 1129 cm^{-1} assigned to this mode in IR. The bands at 574 cm^{-1} in IR is attributed to the in plane vibration of O-C=O group.

3.2.5 OH Group vibration:

Normally in organic molecules strong hydrogen bonds are formed between the protonated amino group and the carboxylic group. O-H stretching vibrations are observed at 2622 cm^{-1} in IR and 3120 cm^{-1} , 2501 cm^{-1} in Raman spectrum.

3.2.6 Vibrations of the skeleton and lattice:

The skeletal vibration of organic acids is all coupled together because of asymmetric motion of a branched carbon atom against its neighbors. The C-C skeleton has characteristic wave number in the range 1132 cm^{-1} - 885 cm^{-1} . In Pyridinium Tartarate crystal, C-C stretching modes were identified as weak bands at 1130 cm^{-1} , 1090 cm^{-1} , 992 cm^{-1} , 896 cm^{-1} in Raman and 1129 cm^{-1} , 1080 cm^{-1} , 987 cm^{-1} in IR. The bands below 200 cm^{-1} in IR and Raman are due to the lattice vibrations.

IV. Conclusion

In the present study, single crystal of Pyridine with Tartaric acid was grown successfully using solution growth method. The FTIR and FT Raman spectra are recorded and complete vibrational assignments were made to identify the presence of functional groups of the grown sample. The molecules of the grown crystal are held together by hydrogen bonds in addition to Van der Waals interactions. The packing of the ions is stabilized by three-dimensional hydrogen-bonded network[5]. The Pyridinium N atom is involved in a rather strong hydrogen bond with O atoms of the carboxylate anion. The Structure may be described as an inclusion complex with the semi-tartrate anion as the host and the Pyridinium cation as the guest. The downshifting of the wave numbers of stretching modes and corresponding increase in the wave number of bending modes of vibration conform the presence of hydrogen bonding features in the crystal.

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