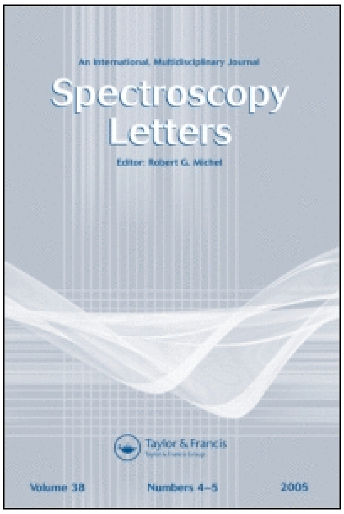

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Infrared Spectra of Inorganic Hydrogen Bond Complexes of Pyridoxine

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To cite this Article Marques, Sergio and Bueno, Willie A.(1996) 'Infrared Spectra of Inorganic Hydrogen Bond Complexes of Pyridoxine', Spectroscopy Letters, 29: 8, 1523 — 1530
To link to this Article: DOI: 10.1080/00387019608007142
URL: http://dx.doi.org/10.1080/00387019608007142

SPECTROSCOPY LETTERS, 29(8), 1523-1530 (1996)

INFRARED SPECTRA OF INORGANIC HYDROGEN BOND COMPLEXES OF PYRIDOXINE

Key words: Hydrogen Bond, Infrared Spectroscopy

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ABSTRACT

Hydrogen bonded compounds obtained between the base Pyridoxine and Hydrogen Chloride, Hydrogen Bromide, Hydrogen Iodide and Nitric Acids are studied by IR Spectroscopy, in the region from 4.000 to 400 cm^{-1}, in the solid state. Results show that there was formation of hydrogen bonded complex between Pyridoxine and the respective acids. Hydrogen Chloride is bonded to Pyridoxine through its N group while the other acids are bonded to its ring. It was still verified low intensity vibrations for the halogenated ions and medium to strong bands for the nitrate ion. In the presence of inorganic acids, Pyridoxine is found in the "enolic" form, once the ν (CO^-) band is not observed.

INTRODUCTION

Pyridoxine is a chemical compound which has three donor centers and one receptor center to the formation of complexes with metallic and rare earth ions [1,2,3,4], organic donors compounds and hydrogen bonded compounds [5,6,7]. Having weak or medium forces these centers permit a variety of situations in the presence of organic and inorganic acids. For instance, J. S. Plant *et al* [7] have studied the formation of hydrogen bonds of Pyridoxine and concluded that the hydrogen bond presents two possibilities of bonding (N-H...Cl and N...H-Cl) due to its tautomeric form.

In this work, one has obtained hydrogen bond complexes in the solid state and has observed the behavior of the receptor centers of Pyridoxine in the presence of the following proton donors: HCl, HI, HBr and HNO_3 for us to try to understand the proton receptor nature of the Pyridoxine molecule.

EXPERIMENTAL

Pyridoxine (Aldrich Chem. Co) was acquired in pure and Hydrogen Chloride forms. The inorganic acids, in water solution, were heated to ~ 330 K in a flask and taken to another flask through a hose, where they met a carbon tetrachloride and chloroform solution at 10:1 molar ratio which contained a known amount of Pyridoxine. The solution is chilled and the solvent was left to evaporate. The obtained crystals were dried at ~ 2 tor vacuum and 310 K, in vacuum desiccator. These crystals were handled in dry ambient or in presence of nitrogen and absence of light. The infrared absorption spectra were obtained in an FTIR Nicolet Spectrophotometer Model 5ZDX. It was used KBr windows and the samples are emulsificated in fluorolube or nujol.

RESULTS AND DISCUSSION

Table I shows the melting points and the absorption bands of the infrared spectra. Figure 1 shows the absorption spectra in the 4000 to 400 cm^{-1} for Pyridoxine and its hydrogen bonded complexes. The attributions were done basing on the band alterations with deuteration, in the dissolved compound, in the complex formation and from literature [08,09] .

TABLE I. Absorption bands of IR Spectra, in the 4000 a 400 cm^{-1} region, of Pyridoxine and yours H bond complexes (in cm^{-1})

Pyridoxine	+ HCl	+ HBr	+ HI	+ HNO_3	Attributions
3525	3540				$\nu N^{+}...H$
	3488				OH_{free}
3379	3326	3390	3386	3395	$\nu(OH...)$
3346	3281	3364	3368	3369	
3281	3161	3337	3319	3346	
				1735	$\nu(NO_3)$
1424	1414	1412	1414	1411	$\delta(OH)$
				1377	$\nu_a(NO_3)$
				1363	$\nu_s(NO_3)+\nu CN$
1341	1327	1351	1358		$\nu(CN)$
1215	1216	1216	1232	1215	$\nu(CO)$
1093					$\nu(CO')$
				1033	$\delta(NO_3)$
915		920	922	912	$\gamma(OH)$
433	389	362	-	-	M.P. (K)

Proton Bonded Complexes

Figure 1 and Table I show that the infrared spectra of crystals, obtained by mixing Pyridoxine with proton donors, have considerable alterations when compared to pure compounds mainly at the OH group bands of the proton donors. This fact, associated to fusion temperature variations, lead us to conclude that there has been formation of proton bonded complexes with HCl, HBr, HI and HNO_3.

Complexes or salts of Pyridoxine and inorganic proton donors

Hydrogen Chloride Complex

The infrared absorption spectrum of Pyridoxine : Hydrogen Chloride complex (Fig. 1B) shows, above 2000 cm^{-1}, the existence of a large absorption band that ranges from ~ 3700 cm^{-1} to ~ 1900 cm^{-1}. This large band contains several submaxima, which is characteristic of compounds with weak to medium hydrogen bonds [10] . There is still the stretching bands of the free OH bond at

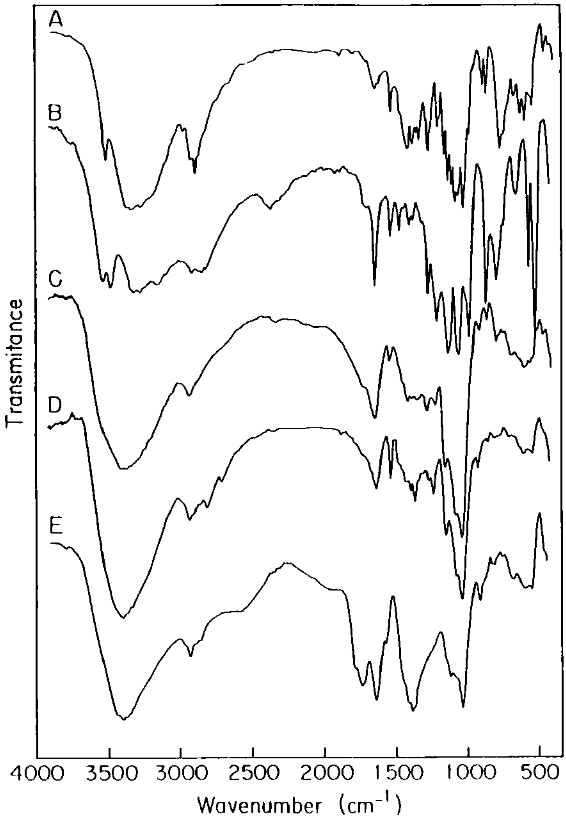

FIGURE 1- Absorption Spectra in the 4000 to 400 cm^{-1} region of Pyridoxine (A) and its Hydrogen bond complexes (1:1) with B) Hydrogen Chloride, C) Hydrogen Bromide, D) Hydrogen Iodide and E) Nitric Acid.

3488 cm^{-1} and the shift of the ν (N$^+$...HCl) band to 3540 cm^{-1}. Bands at 3326, 3281 and 3161 cm^{-1} were shifted to 2358, 2300 and 2243 cm^{-1} after deuteration. These bands can be attributed to ν (OH) which form intra or intermolecular hydrogen bonds. The band at 1414 cm^{-1} was attributed to δ (OH) and the band at 1327 cm^{-1} to ν (CN). The band at 1216 cm^{-1} was attributed to ν (CO). When the complex is formed the band at 1093 cm^{-1}, attributed to ν (CO$^-$)

[11] in Pyridoxine, disappears and a new band at 3488 cm^{-1} attributed to ν (OH) of the C(5)OH group takes place. As well, there has been the shift of the Pyridoxine ν (N^+...HCl^-) band to a region of bigger wave number due to the strong character of nitrogen acid bond. However, the obtained spectrum did not seem as a salt spectrum, so that the proton donation is partial. From these results one can conclude that Pyridoxine formed as proton bonded complex with Hydrogen Chloride, through the nitrogen and hydrogen atoms of the acid in the N^+...H-Cl form.

Hydrogen Bromide Complex

The absorption spectrum at the infrared region for the complex obtained between Pyridoxine and Hydrogen Bromide (Fig. 1C) shows that the band at 3525 cm^{-1} attributed to free ν (N^+...H) in Pyridoxine disappears. There is a shift of the ν (OH) bands of the pure compound to the region of larger wave number. Thus, bands at 3379, 3346 and 3281 cm^{-1} of Pyridoxine shift to 3390, 3364 and 3337 cm^{-1} with the complex formation. The band attributed to δ (OH) in Pyridoxine was shifted to 1412 cm^{-1} in the complex. The band at 1351 cm^{-1} was attributed to ν (CN) and the band at 1216 cm^{-1} was attributed ν (CO). The band at 920 cm^{-1}, attributed to γ (OH) remains stable. Also there has been the disappearance of the ν (CO) [11] band and the spectrum shows the existence of the COH group, that is, Pyridoxine is present at its most stable form. One observes that the ν(N^+...H) free vibration attributed to Pyridoxine at 3525 cm^{-1} disappeared as the complex has been formed, and that is due to its new structural form and the influence of the Br^- ion size on the structure of Pyridoxine, mainly in the ring. In this case one has concluded that there has not been the formation of N^+ ...HBr but only the formation of hydrogen bond. Thus, one can observe that Pyridoxine has formed a proton bonded complex with Hydrogen Bromide through the nitrogen atoms of Pyridoxine and the hydrogen of the acid: N...HBr [12].

Hydrogen Iodide Complex

Results obtained from the spectrum between Pyridoxine and Hydrogen Iodide (Fig. 1D) show the disappearance of 3525 cm^{-1} band of Pyridoxine attributed to ν (N^+...H) free and the shift of the ν (OH) bands to 3386, 3368 and 3319 cm^{-1}, forming the complex. Bands at 1414 and 922 cm^{-1} were attributed to δ (OH) and γ (OH) and the band at 1358 cm^{-1} was attributed to ν (CN).

As in the preceding cases, there has been the disappearance of the 1093 cm^{-1} band attributed to the ν (CO^-) [11] in Pyridoxine, confirming that Pyridoxine is present at its most stable form. One observes the disappearance of the 3525 cm^{-1} band attributed to ν (N^+...H) in the Pyridoxine due to the strong influence of the I atom over the Pyridoxine spectrum. The hydrogen bond obtained is in the N...HI form [12].

Nitric Acid Complex

The spectrum of the obtained complex between Pyridoxine and Nitric Acid (Fig. 1E) shows the disappearance of the band at 3525 cm^{-1} attributed to the ν (N^+...H) of Pyridoxine and the shift of the ν (OH) vibration to the region of greater frequency at 3395, 3369 and 3346 cm^{-1} in the complex. The band at 1735cm^{-1} was attributed to ν (NO_3). Bands at 1411 and 912 cm^{-1} were attributed to δ (OH) and γ (OH) and bands at 1377 and 1364 cm^{-1} were attributed to ν_{as} (NO_3) and ν_s (NO_3). There has not been the appearance of the band at 1093 cm^{-1} attributed to ν (CO^-) [11] in the Pyridoxine. The band at 1033 cm^{-1} was attributed to δ (NO_3^-). One can conclude that Pyridoxine has formed a bonded proton complex with Nitric Acid. The NO_3 anion spectrum There is not the formation of the N^+...HNO_3 type but simply the formation of N...HNO_3 the hydrogen bond [12].

CONCLUSIONS

The formation of compounds with Pyridoxine, in the solid state and in the "enolic" form, causes the appearance of low intensity vibrations for the halogen ions and medium to strong intensity bands for the nitrate ion.

The Hydrogen Chloride presented the same features of 4 - Nitrophenol and 3 - Nitrophenol [12], that is, a shift of the ν (N^+...H) vibration to a larger wavenumber region and the appearance of ν (OH) vibration at approximately 3488 cm^{-1}. Complexes with Hydrogen Bromide, Hydrogen Iodide and Nitric Acid have had the band at 3525 cm^{-1} disappeared and the ring vibrations changed due to the influence of the Br, I and NO_3 anions the large atomic radii of the anions influence the aromatic nucleus of the Pyridoxine molecule. Therefore, one observes that Pyridoxine prefers to bond the Hydrogen of the acid through its N(1) group. In the cases of Hydrogen Bromide, Hydrogen Iodide and Nitric Acid, the anions remain next to the ring and hydrogen bond occurs on it the (XH...π) form, as it happens in other cases [12].

ACKNOWLEDGMENTS

The authors are thankful to FAPESP, CNPq and PADCT for financial support.

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Received: April 18,1996
Accepted: June 24, 1996