

Synthesis and Characterization of Mixed Zinc(II) Complex of Ascorbic Acid
and Thiamine Hydrochloride

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Abstract

Mixed zinc(II) complex of ascorbic acid and thiamine hydrochloride has been prepared and characterized using melting point, conductivity test, thin layer chromatography, infrared, ultraviolet/visible, proton magnetic resonance spectroscopic methods.

The results of the physical and spectroscopic data support the formation of the complex. Ascorbic acid coordinates through the oxygen of the carbonyl group and that of the enolic C-2 hydroxyl group while thiamine hydrochloride coordinates through (N-1) position of the pyrimidine ring.

Keywords: Zinc(II), Mixed complex, Ascorbic acid, Thiamine Hydrochloride.

Introduction

Vitamin is useful in food industry as food additives(Kangi and Seong-geun, 2003). The study of vitamin-metal complexes is increasingly importance in drug design and nutrition(Wasi and Singh, 1987). However, metal complexes play an essential role in pharmaceutical industry and in agriculture(Hariprasath et al, 2010). The metallo-elements present in trace quantities play vital roles at the molecular level in living system. The transition metal ions are responsible for proper functioning of different enzymes(Hariprasath et al, 2010).

Ascorbic acid (vitamin C) is a water-soluble antioxidant. It is used as food additives and in a number of isomeric products to protect the skin from environmental damages and photo aging. Some metal complexes of ascorbic acid have been prepared as reported in (Jab and Gaube, 1984; Maslowska and Owczarek, 1985; Obaleye and Orjiekwe, 1983; Dixon et al, 1995).

The disadvantage of ascorbic acid is its chemical instability in aqueous solution where it becomes quickly oxidized and denatured. Some metal complexes of thiamine hydrochloride have also been reported in literature (Cramet et al, 1981; Gary and Adeyemi, (1981); Cramer et al, 1984; Hadjihadis and Yannopoulos (1983)).

In order to improve the quality of ascorbic acid and its metal complexes, its mixed complex with thiamine hydrochloride has been prepared. We decided to use zinc(II) salt as the sources of the metal ions because it is known that zinc is an important dietary element(Lee, 1996). Hence, we report the synthesis and characterization of mixed zinc(II) complex of ascorbic acid and thiamine hydrochloride.

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Materials and Method

Metal salts ($\text{ZnCl}_2 \cdot \text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) used for the synthesis were obtained from British Drug House Chemical Limited (BDH), England and were used as supplied. Ascorbic acid (vitamin C) and Thiamine hydrochloride (Vitamin B₁) were obtained from Swiss Chemical Limited, Lagos, Nigeria. This study was carried out in the Department of Chemistry, University of Ilorin, Ilorin, Nigeria.

Synthesis of Mixed complexes

The complex was prepared according to the previous literature reports by Abd El-wahab and El-sarrag (2004) with slight modification. 5 mmols of metal salts ($\text{ZnCl}_2 \cdot \text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) was dissolved in 10ml of methanol, followed by addition of (3.372g, 10 mmols) of thiamine hydrochloride and (1.761g, 10 mmols) of ascorbic acid. The mixture were refluxed for 3hr and left for a few days.

In the case of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, no precipitate was formed after keeping the solution for 2 weeks. The filtrate and precipitate from ZnCl_2 was analyzed to determine its composition and structure.

Physical measurements

Infrared spectra in the range $4000\text{--}400\text{cm}^{-1}$ were obtained from samples in the form of KBr pellets using Unicam FTIR spectrometer. The UV/Visible spectra of the samples were run on the Aquamate V4.60 UV/Visible spectrophotometer using methanol/distilled water as solvent. The content of zinc was determined by atomic absorption spectroscopy with Alpha 4 spectrometer.

The proton magnetic resonance (HMNR) spectra was recorded on AV 400 BRUKER NMR Spectrometer at a basic frequency of 200MHz using deuterated chloroform as solvent.

Results and discussion

The ZnCl_2 react with the ligands (L_1 =ascorbic acid, L_2 =thiamine hydrochloride) according to the proposed general equation $[\text{M}(\text{Th})(\text{Asc})(\text{H}_2\text{O})]$. The complex was soluble in distilled water, methanol but insoluble in non polar solvents such as benzene, chloroform, DMSO. The complex decomposed above 360°C . The high melting point confirms formation of the mixed complex.

Table 1: Some physical properties of mixed Zinc(II) complex of Ascorbic acid and Thiamine hydrochloride.

Compound	Colour	M.pt ($^\circ\text{C}$)	% yield	Rf	%metal calc (found)
Ascorbic acid (Asc)	White	190-192	-	0.61	-
Thiamine hydrochloride (Th)	White	244-246	-	0.56	-
$\text{Zn}(\text{Asc})(\text{Th}) \cdot \text{H}_2\text{O}$	White	360	46.0	0.96	8.5(9.3)

The result of the physical data confirm the formation of the mixed complex.

Table 2: Selected IR data of mixed zinc(II) complex of Ascorbic acid and Thiamine hydrochloride.

Ligand/complex	$\nu(\text{N-H})/\text{O-H}$	$\nu\text{C=O}$	$\nu\text{C=N}$	O-H bonding	$\nu\text{M-N}$	$\nu\text{M-O}$
Thiamine HCl	3352(m) 3144(m)				773(s)	-
Ascorbic acid	3874(w)	1763(s)				-
Zn(Th)(Asc) H ₂ O	3374(w) 3204(w,b) 3069(w)	1681(w) 1618(m) 1605(m)			547(m) 521(m)	447(m) 427(s) 416(s)

m=medium, w=weak, s=strong, b=broad.

Table 3: UV/Visible spectra of mixed zinc(II) complex of Ascorbic acid and thiamine.

Ligand/complex	wavelength (nm)	Energy (cm ⁻¹)	Assignment
Thiamine HCl (Th)	234 298	42735 33557	n → π*
Ascorbic acid (Asc)	254	39937	π → π*
Zn(Th)(Asc)(H ₂ O)	315	31746	Charge - transfer

Infrared spectra

The infrared spectra of the free ligands were compared with that of its mixed complex. The N-H/O-H vibrations in the free ligands have been shifted in the mixed complex due to complexation (David, 2000; Brvice, 2001).

The bands at 547cm⁻¹ and 521cm⁻¹ which could not be traced to free thiamine HCl has been assigned to M-N due to coordination through the nitrogen atom (N-1) position of the pyrimidine ring. The M-O stretching frequency is assigned to the bands at 447cm⁻¹, 427cm⁻¹ and 416cm⁻¹ due to coordination through the oxygen of the carbonyl group and that of enolic C-2 hydroxyl group (Lever, 1984).

UV/Visible spectra

The UV/Visible spectra of the free ligands were compared with that of its mixed complex Zn(Asc)(Th)(H₂O). The zinc(II) complex show one absorption band at 315nm (31746cm⁻¹) assigned to metal - ligand charge transfer (Lawal, 2010).

Hnmr spectra

The complex, Zn (Asc) (th) (H₂O) was insoluble in deuterated chloroform, hence the Hnmr spectra shows mainly the solvent peaks. On the basis of the spectroscopic data obtained, In the absence of X-ray crystallographic data, the structure tentatively proposed for mixed thiamine-ascorbate complex is shown in figure 1 below:

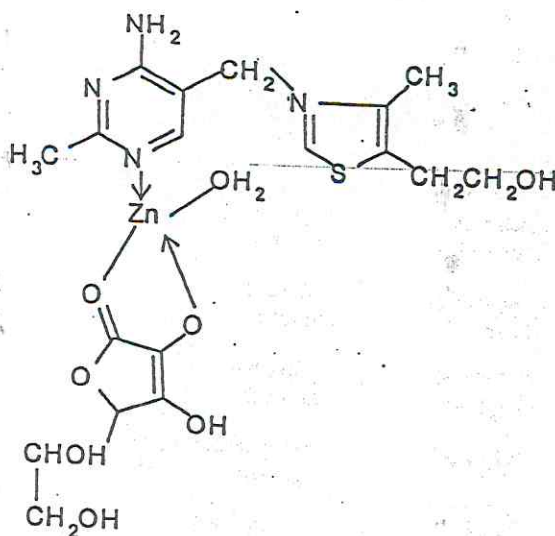


Fig 1: Proposed Structure for Mixed Thiamine-Ascorbate Metal Complex

Conclusion

It is confirmed from the physical and spectroscopic data that zinc(II) form mixed complex with ascorbic acid and thiamine HCl.

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