

STUDIES OF THE POLYNUCLEAR COMPLEXES OF LABILE LIGANDS OF VITAMIN B₁ AND Zn (II), Cd (II) AND Hg (II) WITH Fe (III)

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The ligands (complex salts) of vitamin B₁ (H Vit.) and the chlorides of Zn, Cd and Hg with the general formula, [HVit]⁺² [MCl₄]⁻² were prepared and their interactions with iron (III) investigated. It was found that the complex salts of Zn and Cd produced the dinuclear complexes and that of mercury produced a complex without the thiamine moiety. The possible reason for the absence of a Hg complex similar to those of Zn and Cd may be that large size of mercury ion. The complexes were characterized by elementary analyses, infrared and visible spectra, magnetic moment and conductivity measurements.

Key words: Vitamin B₁, Ligands, Elementary analyses, Conductivity measurements, Dinuclear complexes.

Introduction

Vitamin B₁ also called thiamine chloride hydrochloride (Fig 1) is very important in humans. Its potential as a ligand is being exploited in coordination chemistry chiefly because of its wide variety of coordination sites (Talbert *et al* 1970). The great success achieved in the exploitation of the coordination chemistry of vitamin B₁ is owed to the recovery of acetate catalyzed removal of the pyrimidinyl hydrogen ion of NH₂ group of vitamin B₁ moiety (Adeyemo and Shamin 1983a). Many of the reported complexes of thiamine are bounded by metals through the N(1') of the pyrimidine ring (Adeyemo *et al* 1983b).

Recently, a number of complexes have been reported (Casas *et al* 1995) indicating the metal bonding through the oxygen of the hydroxyethyl group. Also of great interest are the reported polymetallic complexes (Adeyemo 1986; Ojo 2001).

Polymetallic complexes of vitamin B₁ involving Fe (III) have not been investigated as yet. This communication now reports

its dinuclear complexes of vitamin B₁ involving Zn (II), Cd (II) with Fe (III) and discusses the inability of Hg (II) to produce similar dinuclear complex.

Materials and Methods

Preparation of the labile ligands (complex salts). Ligand were prepared by adding a solution of thiamine chloride hydrochloride (3.37g, 0.01 mol) in 50 ml distilled water to a 0.01M solution of the metal (Zn, Cd and Hg) chloride. The resulting mixture was stirred magnetically and refluxed for 3h. The precipitate obtained in each case was filtered, washed with distilled water, dried and finally analyzed. The complex salts conform to the formula [H Vit]⁺² [MX₄]⁻² with HVit. = protonated thiamine and X = Cl⁻.

Preparation of the complexes. The complexes were prepared by adding the labile ligands, [H Vit]⁺² [MX₄]⁻², [M = Zn, Cd or Hg] (0.01 mol) to a methanolic solution of iron (III) hydroxyl acetate (0.01 mol), refluxed and stirred magnetically for 3h. The resulting precipitate was filtered, washed with methanol and recrystallized from methanol and subsequently dried in vacuum.

Physical measurements. Elemental analyses were carried out at micro-analytical laboratory, University of Ibadan. The metal ions were determined by complexometric titration. The infrared spectra of the ligands and complexes were recorded on a PYE - UNICAM SP 300 spectrophotometer, electronic spectrophotometer, were recorded on a SP 500 spectrophotometer, magnetic susceptibility data were recorded on Gouy's balance using Hg [Co(NCS)₄] as calibrant, and molar conductance on a conductivity bridge with a cell constant 1.0 cm⁻¹ mol⁻¹.

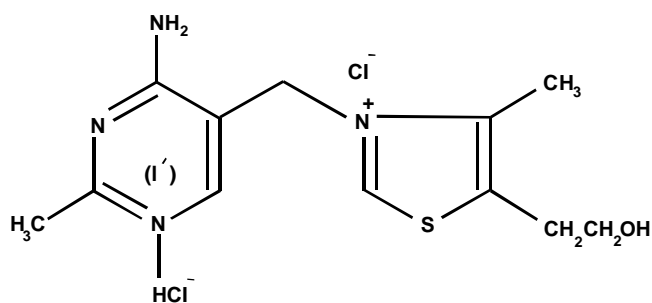


Fig 1. The structure of thiamine chloride hydrochloride (Vitamin B₁).

Table 1
Analytical and molar conductivity data for the complexes

Complex	Found (Calcd).(%)					Molar conductivity	
	C	H	N	Cl	Fe	M	$\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
[(Vit) FeZnCl ₅] .2H ₂ O	22.69 (22.68)	3.95 (3.31)	8.85 (8.82)	33.53 (33.54)	9.00 (8.82)	10.38 (10.24)	35.10
[(Vit) FeCd Cl ₅] .2H ₂ O	22.32 (22.91)	3.38 (3.02)	8.75 (8.91)	27.33 (27.46)	8.34 (8.21)	19.00 (18.52)	42.86
[HgFe ₂ (OH) ₂ (Ac) ₄] .3H ₂ O	15.09 (15.09)	4.58 (3.13)	--- ---	--- ---	17.53 (17.48)	33.13 (31.58)	19.59

Vit, Vitamin B₁ ligand (thiamine); M, Zn (II), Cd(II) or Hg(II); Ac, CH₃COO⁻

Table 2
Infrared data for the ligand and complexes (cm⁻¹)

	v(O - H)	v(N - H)	$\delta(\text{NH}_2) +$ pyrimidine ring	v _{asy} (COO) +	v(M - N) +	v(M - O) +	v(M - Cl)	v(M - M)
[HVit] ⁺² [MCl ₄] ⁻²	3450	3270	1650	---	---	---	---	---
[(Vit)FeZnCl ₅]Cl .2H ₂ O	3389	3222	1643	---	---	600	450	250v.w
[(Vit)FeCdCl ₅]Cl .2H ₂ O	3412	3206	1628	---	---	600	400	240v.w
[HgFe ₂ (OH) ₂ (Ac) ₄] .3H ₂ O	3500 2500(v.br)	---	---	1600 1400	---	560(v.br)	---	230v.w

M, Zn(II); Cd(II) or Hg(II) from labile ligand [HVit]⁺² [MCl₄]⁻²

Results and Discussion

Nature and stoichiometry. All the complexes are brown in colour with the exception of mercury, which was dark brown in colour. The analytical data (Table 1) show that thiamine is present in the zinc (II) and cadmium (II) complexes but not that of mercury (II). This may probably be due to steric factors arising from the sizes of the Hg (II), thiaminium and acetato ligands. The molar conductivity values (Table 1) of ~35 and ~43 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ show the zinc and cadmium complexes as 1:1 electrolyte in dimethyl sulphoxide (DMSO) while a value of ~20 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ shows the non-thiamine coordination mercury complex as a non-electrolyte in DMSO (Geary 1971; Rajavel and Krishnan 1998).

Infrared spectra. The IR results are shown in Table 2. In the labile ligands, two bands observed at 3450 and 3270 cm⁻¹ are assigned to v(O - H) and v(N - H) vibrations, respectively (Adeyemo *et al* 1983; Ojo 2001).

Two other strong bands at 1650 and 1600 cm⁻¹ are assigned for coupling of the pyrimidine ring and $\delta(\text{NH}_2)$ vibrations, respectively while the band at 1554 cm⁻¹ is assigned for pyri-

midine ring vibrations. In the complexes, the following changes are observed. The band at 3450 cm⁻¹ shifts to 3389 cm⁻¹ and 3412 cm⁻¹ in the zinc and cadmium complexes, respectively. In the mercury complex, it is replaced by a very broad band at 3500 - 2500 cm⁻¹. The band at 3270 cm⁻¹ assigned to v(N - H) in the ligands shifts to 3222 and 3206 cm⁻¹ in the zinc and cadmium complexes, respectively. This band is absent in the mercury complex, thus indicating the absence of thiamine moiety in the complex. The band at 1650 cm⁻¹ assigned to the coupled pyrimidine ring and $\delta(\text{NH}_2)$ vibrations shifts to 1643 and 1628 cm⁻¹ in the zinc and cadmium complexes, respectively but it is absent in the mercury complex, which further supports that thiamine is absent in the mercury complex. Two new bands at 1600 and 1400 cm⁻¹ absent in the ligands are observed in the mercury complex, and have been assigned to v_{asy} (COO) and v_{sy} (COO) vibrations. A weak band at about 300 cm⁻¹ which has been assigned to v(M-M) (metal-metal) vibration is observed in all the complexes (Nakamoto and Keif 1967; Ferraro 1971; Adeyemo *et al* 1983b; Onoa *et al* 1999; Bien 1999; Ojo 2001).

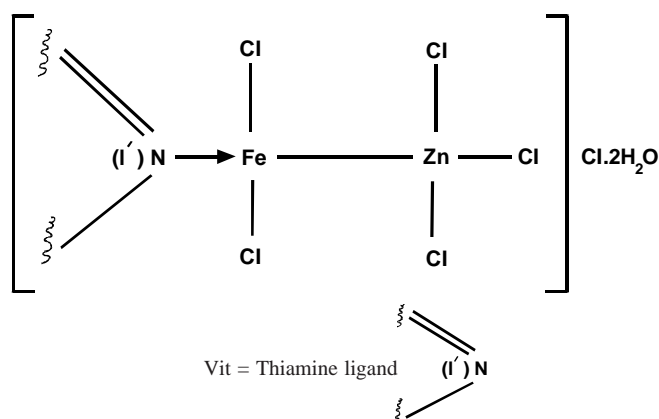


Fig 2. The structure of $[(\text{Vit}) \text{FeZnCl}_5] \text{Cl} \cdot 2\text{H}_2\text{O}$.

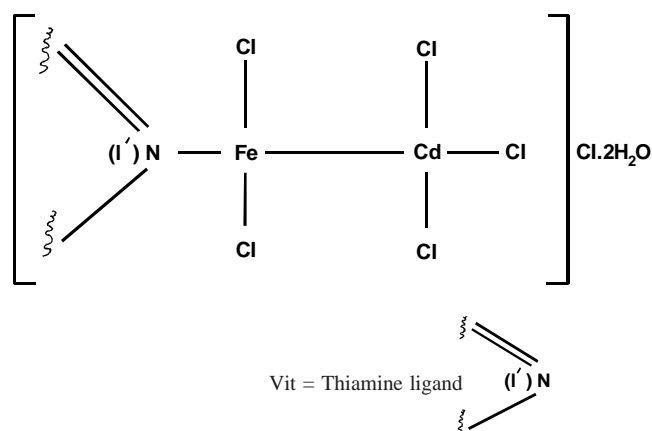


Fig 3. The structure of $[(\text{Vit}) \text{Fe Cd Cl}_5] \text{Cl} \cdot 2\text{H}_2\text{O}$.

Magnetic moment. All the complexes contain iron(III) with the values of 11.6, 10.7 and 11.5 B.M. for the zinc, cadmium and mercury complexes, respectively. These are exceedingly too high values for systems containing five unpaired electrons. The observation can only be rationalized on the basis of an existing cooperative paramagnetism (ferromagnetism) between the neighbouring iron (III) ions in the crystal lattice arising from the parallel alignment of the magnetic dipoles of the individual ions (Earnshaw 1968; Shriver *et al* 1990).

Electronic spectra. The complexes show no significant absorptions in the visible region. This is consistent with a d^5 tetrahedral electronic configuration which is not expected to exhibit spin forbidden d-d transitions since all tetrahedral complexes are energetically favoured to be high spins. The octahedral, weak, spin-forbidden bands such as ${}^2T_{1g} \leftarrow {}^6A_{1g}$ would have been observed in the visible region if the complexes were not tetrahedral (Purcell and Kotz 1999). Based on the above information, the structures as shown in Fig. 2, 3 and 4 have been proposed for the complexes.

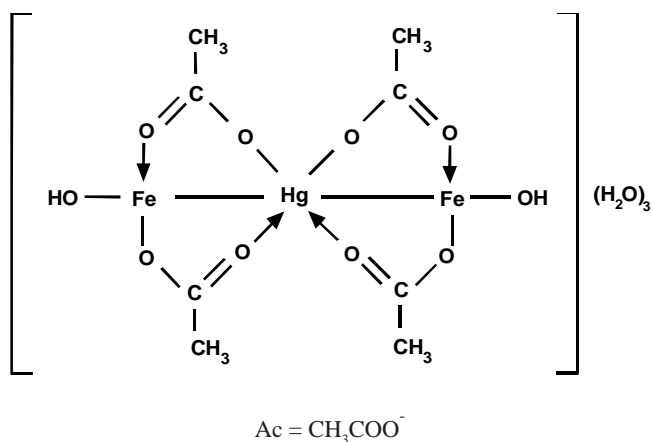


Fig 4. The structure of $[\text{HgFe}_2(\text{OH})_2(\text{Ac})_4] \cdot 3\text{H}_2\text{O}$.

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