Short Communication

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LOW SPIN TRINUCLEAR COMPLEXES OF LABILE VITAMIN B_1 WITH COBALT (II)

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Thiamine chloride hydrochloride (Fig 1), vitamin B_1, is a very versatile ligand due to its variety of coordination sites (Talbert *et al* 1970). The pioneering studies on thiamine complexes led to the synthesis of only ionic complexes or salts of the type $[HT]^{2+} [MX_4]^{2-}$ with no direct metal-nitrogen bonds (White and Drago 1971) due to the relative ease of protonation of the pyrimidine N(1') which was later overcome with the discovery of acetate buffer systems (Adeyemo and Shamin 1983a). Later work (Adeyemo *et al* 1986) on thiamine led to the synthesis of dinuclear and trinuclear complexes with metal-nitrogen and metal-metal bonds, and recently, a dimeric cadmium-thiamine complex has been prepared (Casas *et al* 1995). The present work was undertaken to investigate the ability of cobalt in forming polymetallic complexes with vitamin B_1, and interestingly the present communication has positively revealed it.

Ligands were prepared by dissolving thiamine chloride hydrochloride (3.37g, 0.01 mol) in 50 cm^3 of distilled water and added to a solution (0.01 mol) of the metal (II) (Zn,Cd & Hg) salts with the mixture stirred magnetically and refluxed for 3h. The precipitate in each case was filtered, washed with methanol, recrystallized from methanol, finally dried *in vacuo* and analysed. They all conform to the formula $[HT]^{2+} [MX_4]^{2-}$ with T = Thiamine and X = Cl^-.

Metal complexes were prepared by interacting methanolic solution of cobalt (II) acetate dihydrate (2.13g, 0.01 mol), with the ligands in a 1:1 mole ratio and the mixture in each case refluxed and stirred magnetically for 3h. The precipitate formed was filtered, washed with methanol, recrystallized from methanol, dried in vacuo and subsequently analysed. Elemental analysis (Done at Micro-analytical Laboratory, University of Ibadan) I.R. spectra (recorded on a PYE-UNICAM SP 300 spectrophotometer), electronic spectra (recorded on a SP 500 Spectrophotometer), magnetic susceptibility (recorded on a Gouy's Balance) and finally conductance were used to characterize the complexes.

The elemental analysis and conductivity of the complexes are given in Table 1. The low conductance values in the range 20-24 ohm^{-1} cm^2 mol^{-1} indicate the complexes as non-electrolyte in DMSO (Geary, 1971). The I.R spectra of the complexes are reported in Table 2. The labile ligands show two bands at 3450 and 3270 cm^{-1} assigned to ν(O-H) and ν(N-H) vibrations. Two other strong bands at 1650 and 1600 cm^{-1} range are assigned to coupling of the pyrimidine ring and $\delta(NH_2)$ vibrations while the band at 1554 cm^{-1} is assigned to pyrimidine ring vibration. In the complexes, the band at 1650 cm^{-1} shifts negatively by nearly 20 cm^{-1} while the band at 1554 cm^{-1} shifts to 1540 cm^{-1} indicating the involvement of the pyrimidine N (1') in coordination. The complexes show new bands at 320 cm^{-1} (v.w.), 410 cm^{-1} and 510-520 cm^{-1} and are assigned to ν_{bridge}(M-Cl), $\nu_{term.}$(M-Cl) and ν(M-N) vibrations respectively (Adeyemo *et al* 1983b; Ferraro 1971; Kief and Nakamato 1967 Onoa *et al* 1999). The magnetic moments and the electronic absorption spectrum for the complexes are shown in Table 3. The observed magnetic moments are in the range 1.75-1.86 B.M. which indicate the cobalt (II) to be low spin. The values even though higher than expected for a single electron can be ascribed to spin-orbit coupling (Earnshaw 1968). The complexes exhibit two absorption bands in the regions 11500-12500 cm^{-1} (ν_1) and 15385-16395 cm^{-1} (ν_2) of low intensities and have been assigned to $^2E_g \rightarrow {}^2T_{1g} \rightarrow$ and $^2A_{1g}$ transitions respectively (Shriver *et al* 1990).

Based on the above information, the following structure (Fig 2) has been proposed for the complexes.

Table 1

Analytical and molar conductance data for the complexes

Complex	Found (Calcd.)				Molar conductivity
	C	H	N	M	ohm^{-1} cm^2 mol^{-1}
$[(CoTCl_3)_2Zn (Cl)_2]$	28.94	3.40	11.28	22.50	
	(28.89)	(3.41)	(11.23)	(22.56)	23.86
$[(CoTCl_3)_2Cd (Cl)_2]$	27.59	3.26	5.36	22.08	
	(27.68)	(3.32)	(5.41)	(22.03)	23.55
$[(CoTCl_3)_2 Hg (Cl)_2]$	25.42	3.10	17.80	10.45	
	(25.40)	(3.00)	(17.74)	(10.41)	20.81

Table 2
Infrared data for the complexes (cm^{-1})

Complex	ν(O-H)	ν(N-H)	$\delta(NH_2)$ + pyrimidine ring	Pyrimidine ring	ν(M-N) n(M-Cl)
$[(CoTCl_3)_2 Zn (Cl)_2]$	3360s	3200s	1630s 1600s	1540s	510s 410s, 320 v.w
$[(CoTCl_3)_2 Cd (Cl)_2]$	3380s	3200s	1630s 1600s	1540s	520s 410s, 320v.w
$[(CoTCl_3)_2 Hg (Cl)_2]$	3280br	3100m	1630s 1590s	1540s	515s 410s, 320 v.w

Table 3
Electronic spectra and magnetic moment data for the complexes

Complex	Bands (cm^{-1})	vm_{eff}(B.M.)
$[(CoTCl_3)_2 Zn (Cl)_2]$	12500 (v_1) 15385 (v_2)	1.75
$[(CoTCl_3)_2 Cd (Cl)_2]$	12490 (v_1) 15400 (v_2)	1.80
$[(CoTCl_3)_2 Hg (Cl)_2]$	11500 (v_1) 16395 (v_2)	1.86

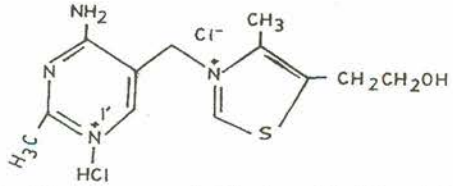

Fig 1. The structure of thiamine chloride hydrochloride (vitamin B_1).

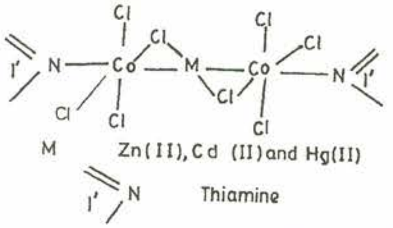

Fig 2. The structure of the complex $[(CoT\ Cl_3)_2M\ (Cl)_2]$.

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