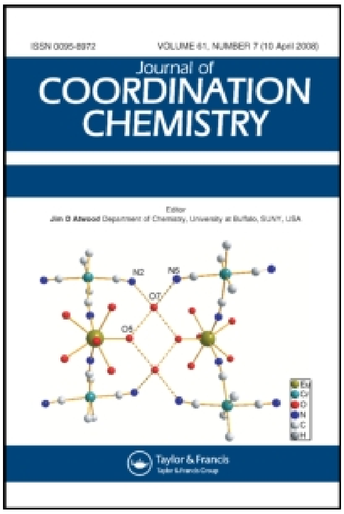

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A COBALT(II) COMPLEX OF VITAMIN B_1

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NOTE

A COBALT(II) COMPLEX OF VITAMIN B_1

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Thiamine (Vitamin B_1) when phosphorylated gives thiamine pyrophosphate (coenzyme cocarboxylase) (Fig. 1) which catalyzes the decarboxylation of α-keto acids. This catalysis is enhanced by the presence of divalent metal ions[1,2] such as Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, *etc.* The relative positions of these metal ions in the catalytic efficiency trend depend on the source of the enzyme. For example, for pyruvate decarboxylase from yeast,[3] the catalytic efficiency is $Mg^{2+} > Mn^{2+} > Co^{2+} > Zn^{2+} > Fe^{2+} > Cd^{2+}$ while for pyruvate decarboxylase from wheat germ,[4] the order is $Mg^{2+} > Co^{2+} > Zn^{2+} > Fe^{2+} > Ni^{2+} > Cd^{2+}$ and from transketolase yeast,[5] the order is $Mn^{2+} > Mg^{2+} > Fe^{2+} > Ni^{2+} > Co^{2+}$. Quite naturally, one would like to know what role each metal ion plays in enzymatic processes.

Since the recognition[3] of the importance of divalent metal ions in the catalytic activity of the yeast pyruvate decarboxylase system in 1932, many proposals have been forwarded. One such proposal is that Mg^{2+} functions as a bridge between the apoenzyme and the coenzyme. It is not unreasonable to suggest that the metal ions hold the cocarboxylase in the most suitable conformation for enzymatic action.

Earlier attempts to prepare cobalt(II)-thiamine complexes in which there is direct metal-ligand bonding had proved abortive.[1,2] Recent reports,[6–10] however, have suggested that almost all divalent metal ions could be incorporated into thiamine and its derivatives, employing an acetate catalyzed method. This work is being extended to the trivalent metal ions in our laboratory and the results will be reported in another paper. In an effort to understand the roles which metal ions play in enzymatic processes, a cobalt(II)-thiamine complex, $Co(Th)Cl_3$, has been prepared and some of its properties determined.

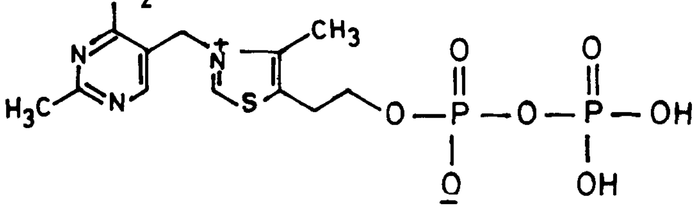

FIGURE 1 Thiaminepyrophosphate (cocarboxylase).

[†] To whom correspondence should be addressed.

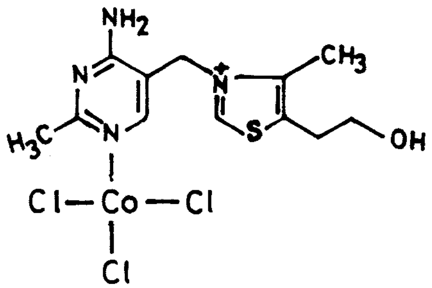

FIGURE 2 Proposed structure of the cobalt(II)-thiamine complex.

EXPERIMENTAL

Thiamine chloride hydrochloride (Vitamin B_1) and deuterium oxide were obtained from the Aldrich Chemical Company while cobalt acetate tetrahydrate was purchased from the Baker Analytical Company. All chemical reagents were used as commercially available without any further purification.

The infrared spectrum was recorded on a Beckman 621 infrared grating spectrophotometer in KBr pellets, and proton NMR recorded on a Nicolet 200 MHz high resolution spectrophotometer. The magnetic susceptibility measurements were carried out by the Gouy method at room temperature using a Newport Instruments Gouy balance. Melting points were determined using a Reichert Austria Instrument equipped with a digital thermometer.

A suspension of 4.98 grams (2.0×10^{-2} mol) of cobalt(II) acetate tetrahydrate in 50 cm^3 methanol was added slowly to a suspension of 6.74 grams (2.0×10^{-2} mol) of thiamine chloride hydrochloride in 50 cm^3 of methanol over a period of 30 minutes with constant stirring at room temperature. The reaction mixture was stirred magnetically for another 3 hours after which it was filtered by suction and the solid was washed with hot methanol, acetone and ether. The intensely blue-coloured compound was dried at room temperature overnight and then in the oven at 120°C for 3 hours.

Anal.: Calcd. for $Cl_3CoC_{12}H_{17}N_4OS$ (yield = 2.60g; M.P. = 212-213°C): Co, 13.69; C, 33.46; H, 3.95; N, 13.01; Cl, 24.73%. Found: Co, 13.72 C, 33.39; H, 3.98; N, 12.98; Cl, 24.79%. Elemental analysis was performed by the Microanalytical Laboratory of Ibadan.

RESULTS AND DISCUSSION

The reaction of thiamine with Co(II) was carried out in methanol since an attempt to obtain the solid cobalt(II)-thiamine complex in aqueous medium proved abortive.[11] This reaction could be represented as follows,

$$\mathrm{ThH}^{2+} + \mathrm{OAc}^- \longrightarrow \mathrm{Th}^+ + \mathrm{HOAc} \tag{1}$$

$$2\mathrm{Th}^+ + \mathrm{Co}^{2+} \longrightarrow \mathrm{Co(Th)}^{3+} + \mathrm{Th}^+ \tag{2}$$

$$\mathrm{Co(Th)}^{3+} + 3\mathrm{Cl}^- \longrightarrow \mathrm{Co(Th)Cl_3} \tag{3}$$

$$\mathrm{ThH}^{2+} + \mathrm{OAc}^- + \mathrm{Co}^{2+} + 3\mathrm{Cl}^- \longrightarrow \mathrm{Co(Th)Cl_3} + \mathrm{HOAc} \tag{4}$$

TABLE I

Some relevant infrared frequencies for thiamine.HCl_2 and its cobalt(II)-thiamine complex

Thiamine.HCl_2	Co(thiamine)Cl_3	Assignment
3450vs	3452vs	
3435vs	3414vs	
—	3331vs	OH, NH_2, CH
3270vs	3234vs	aromatic or aliphatic
3075vs	3089vs	stretchings
1658vs	1644vs)	NH_2 bending + ring
1608s	1614vs)	stretching coupling
	)	
1538s	1593sh)	Skeletal C = C, C = N
1505sh	1552vs)	
	)	
1035vs	1076s	C-OH stretching
	1040m	
—	520w	Co-N(pyrimidine)
—	306m)	
	282m)	Co-Cl
	200m)	

vs = very strong; s = strong; m = medium; w = weak; sh = shoulder.

where ThH^{2+} = thiamine dication, Th^+ = thiamine monocation. Equation (*4*) represents the net reaction and is obtained by adding equations (*1*) through (*3*). Like the Cd(Th)Cl_3 and Zn(Th)Cl_3 complexes reported earlier,[7,10] Co(Th)Cl_3 is soluble in water and dimethyl sulfoxide. The complex is essentially a non-electrolyte in DMF (21.2 ohm^{-1} cm^2 mol^{-1}; 10^{-3} M at 25°C). This observation is in good agreement with earlier reports.[12,13]

The NMR spectrum does not provide much information. However, the broadness of all the signals confirmed that this complex is paramagnetic. A moment of 4.72 B.M. was observed for this complex. This value is higher than the "spin only" value of 3.88 B.M. The difference between the observed and the "spin only" values is due to orbital contribution. This observation is in excellent agreement with all tetrahedrally coordinated Co(II) complexes reported earlier.[14]

Table I lists the relevant infrared frequencies of thiamine.HCl_2 and the Co(thiamine)Cl_3 complex. The very strong bands at 3450, 3455, 3270 and 3075 cm^{-1} in thiamine.HCl_2 are due to OH, NH_2 and CH aromatic or aliphatic stretching motions.[15] In the Co(thiamine)Cl_3 complex, corresponding very strong bands appear at 3452, 3414, 3331, 3234 and 3089 cm^{-1}. The non involvement of OH and NH_2 in bonding is demonstrated by the small shift in the positions of these bands in the complex relative to thiamine.HCl_2. Evidence for coordination *via* the ring nitrogen is reflected in the large shifts in (C = C) and (C = N) modes. In thiamine.HCl_2, these bands appear at 1538 and 1505 cm^{-1} whereas they appear at 1593 and 1552 cm^{-1} in the Co(thiamine)Cl_3 complex. The weak band at 520 cm^{-1} is ascribed to a Co-*N*(pyrimidine) band while the medium bands at 200, 282 and 306 cm^{-1} are attributed to Co-Cl vibrations.

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