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Studies Involving Labile Vitamin B_1 Metal Complexes

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Introduction

Traditionally, Vitamin B_1 is a unidentate ligand, in spite of the wide variety of coordination sites (NH_2, N3′, N1′, S, OH) it has to offer. Numerous investigations have established the fact that the preferred binding site is N1′ position of this ligand [1]. Recently [2, 3], however, we proposed possible coordination of the group 2B metal ions, especially mercury(II), to N3′ and/or NH_2 position. The small ^{13}C and ^1H NMR chemical shifts observed for these complexes led us to the conclusion that such complexes are pseudo-contact or outer-sphere complexes. Earlier, Theophanides *et al.* [1] isolated some stable Pt(II) and Pd(II) complexes of thiamine which are the first examples reported having a direct metal-to-nitrogen bond. As a result of very large chemical shifts in both ^{13}C and ^1H NMR observed for these complexes, these authors claimed N1′ position as the binding site.

In $Hg(Th)Cl_4$, $Cd(Th)Cl_4$ and $Zn(Th)Cl_4$ complexes, N1′ position of thiamine is still open to attack by Pd(II) or Pt(II). As an extension of our previous work [2, 3], this paper reports the interaction of Pd(II) with $Hg(Th)Cl_4$, $Cd(Th)Cl_4$ and $Zn(Th)Cl_4$ labile complexes. It would be interesting to find out what happens in these reactions, since there are two possibilities: (1) displacement reaction whereby Pd(II) displaces Hg(II), Cd(II) and Zn(II) from these complexes and (2) addition reaction whereby Pd(II) adds to these complexes, resulting in the formation of heterodinuclear Vitamin B_1 metal complexes the first of its kind.

Experimental

The synthetic approach of $Hg(Th)Cl_4$, $Cd(Th)Cl_4$ and $Zn(Th)Cl_4$ complexes has been reported [3]. A mixture of warm aqueous solutions of these complexes and K_2PdCl_4 (1:1 mole ratio) instantaneously conveniently afforded new complexes. The precipitate formed in each case was thoroughly washed with cold distilled water, acetone and ether, and finally dried under the hood. The NMR spectra were recorded on high resolution NMR 200 MHz Nicolet instrument with DMSO-d_6 as solvent and TMS as internal reference standard. Elemental analyses were performed by Galbraith Laboratories Inc. of Knoxville, Tennessee. *Anal.* Calcd. for $Hg\cdot Pd(Th)Cl_3$: C, 20.13; H, 2.38, N, 7.83%. Found: C, 20.91; H, 2.89; N, 7.89%. *Anal.* Calcd. for $Pd(Th)Cl_3$(Cd displaced): C, 27.98; H, 3.30 N, 10.88%. Found: C, 28.81; H, 3.91; N, 11.18%. *Anal.* Calcd. for $Pd(Th)Cl_3$(Zn displaced): C, 27.98; H, 3.30; N, 10.88%. Found: C, 28.84; H, 3.91; N, 11.13%.

Results and Discussion

The ^{13}C NMR chemical shifts of thiamine and its complexes are shown in Table 1. The most downfield shifted carbons are C-2′ (4.60 ppm), 2′-CH_3 (6.31 ppm) and C-6′(12.00 ppm), which are adjacent to the N1′ position of the ligand. These results are in very good agreement with the previous work [1]. Although, kinetic studies were not done on these

TABLE I. ^{13}C NMR Chemical Schifts of Vitamin B_1 and Its Metal Complexes (ppm).

Compound	4-CH_3	2′-CH_3	5-α-CH_2	Bridged CH_2	5-β-CH_2
Vitamin B_1	11.63	21.13	29.33	49.88	59.56
$Hg\cdot Pd(Th)Cl_3$	11.50	27.23	29.28	50.38	59.50
$Pd(Th)Cl_3$(Cd displaced)	11.55	27.33	29.28	50.39	59.53
$Pd(Th)Cl_3$(Zn displaced)	11.67	27.44	29.38	50.47	59.56

Compound	C-5′	C-5	C-4	C-6′	C-2	C-4′	C-2′
Vitamin B_1	105.28	135.31	142.13	146.65	155.23	161.23	163.00
$Hg\cdot Pd(Th)Cl_3$	105.57	135.68	142.00	157.55	154.98	161.83	167.30
$Pd(Th)Cl_3$(Cd displaced)	105.39	135.65	142.04	158.43	154.65	161.45	167.64
$Pd(Th)Cl_3$(Zn displaced)	105.47	135.57	142.11	158.65	155.28	16.40	167.73

systems, by mere observation, the relative reactivity order of Pd(II) toward these complexes could be formulated as $Hg(Th)Cl_4 > Cd(Th)Cl_4 > Zn(Th)Cl_4$. Thus it appears that these complexes are already in the deformed states compared to the metal free thiamine. Such deformation may account for the rapidity with which Pd(II) reacted with these labile complexes. While the reactivity order of Pd(II) toward these complexes is very interesting, it is not surprising. This trend may be explained in terms of the polarizability or water exchange rates of these metal ions ($Hg^{II} > Cd^{II} > Zn^{II}$).

Although, Hg(II), Cd(II) and Zn(II) belong to the same group, their Vitamin B_1 complexes react differently with Pd(II). The interaction between Pd(II) and $Hg(Th)Cl_4$ results in the formation of a novel heterodinuclear complex, $HgCl_2 \cdot Pd(Th)Cl_3$, which presumably decomposes in the following manner:

$$HgCl_2 \cdot Pd(Th)Cl_3 \longrightarrow Hg \cdot Pd(Th)Cl_3 + \text{gas} \qquad (1)$$

$$Hg \cdot Pd(Th)Cl_3 \longrightarrow Pd(Th)Cl_3 + Hg \qquad (2)$$

The assumption that a gas was evolved in step (1) is advanced on the ground that the stoppered container became cloudy after a few days of storage. After a couple of months of storage, black precipitate started to separate from the initially yellow complex. The stoppered vial containing $Pd(Th)Cl_3$, on the contrary, remained very clear without any noticeable change in the appearance of this complex. Meanwhile, work is in progress to obtain single crystals of these complexes for X-ray studies as well as exploring the possibility of using $Hg(Th)Cl_4$, $Cd(Th)Cl_4$ and $Zn(Th)Cl_4$ labile complexes in the preparation of more unusual complexes, which would be impossible with metal free thiamine in support of deformation mechanism.

Although, $Pd(Th)Cl_3$ is known [1], the present synthetic approach provides a much faster alternative method for preparing this complex with perhaps a much better yield. The new heterodinuclear complex, $Hg \cdot Pd(Th)Cl_3$, on the other hand, may provide a mechanism whereby mercury poison could be prevented in the biological system. The unusual oxidation state of metal/metals in this complex is under further investigation.

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