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Nuclear Magnetic Resonance Studies of New Organocadmium Compound, Cd(thiamine)Cl_3

ADEGBOYE ADEYEMO*, A. SHAMIM and ANNE TURNER

Department of Chemistry, Howard University, Washington, D.C. 20059, U.S.A.

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In 1977, Theophanides *et al.* reported the discovery, using NMR techniques, of Pt(II) and Pd(II) thiamine complexes [1] which were claimed to be the first examples of complexes having a metal-to-nitrogen bond. The large ^{13}C NMR chemical shifts observed for C-6′ (12–13 ppm) and 2′-CH_3 (4.9–5.5 ppm) carbons which are adjacent to the assumed coordination site led them to the conclusion that Pt(II) and Pd(II) bonded to the thiamine molecule through the N(1′) position of the pyrimidine moiety. Unfortunately, there has been no report of the crystal and molecular structures of Pt(II) and Pd(III) thiamine complexes. Although Cramer *et al.* reported recently [2] the crystal and molecular structure of a thiamine ion bonded to a metal ion, there has been no NMR report of this complex. In this paper, we wish to report NMR data of this new organocadmium complex, Cd(thiamine)Cl_3 whose crystal and molecular structure has been previously reported [2] in the hope of drawing a comparison between the NMR data of Pt(II) and Pd(II) thiamine complexes and those of the new Cd(II) thiamine complex, Cd(thiamine)Cl_3. This report will not only show whether or not the chemical shifts in these complexes are dependent on the metal ions, but will also serve as a guide in establishing the binding site both in situations where suitable crystals could be obtained for X-ray analysis and in situations where obtaining suitable crystals presents a problem.

The new organocadmium complex Cd(thiamine)Cl_3 was prepared by slowly evaporating an aqueous mixture of $Cd(CH_3CO_2)_2$ and thiamine·HCl in a one-to-two molar ratio. It is interesting to observe that Cd(thiamine)Cl_3 obtained using Cramer's method is of the same composition and has an identical NMR pattern and chemical shifts.

Figures 1 and 2 show the ^{13}C NMR spectra of the protonated thiamine and its Cd(II) complex, respectively, while the Table I shows the ^{13}C NMR chemicals shifts. Water was chosen as solvent because both the ligand and the complex are readily soluble in water and also due to the fact that water gives better separation of peaks. The assignment of the peaks was based on previous works [3]. In the protonated thiamine, C-6′, C-2′ and 2′-CH_3 resonances occur at 145.5, 164.1 and 22.0 ppm, respectively, whereas in the Cd(thiamine)Cl_3 complex, the same resonances occur at 157.3, 169.6 and 24.9 ppm, respectively. Thus C-6′, C-2′ and 2′-CH_3 carbons have shifted downfield by 9.8, 5.5 and 2.9 ppm, respectively. These chemical shifts are comparable to those observed

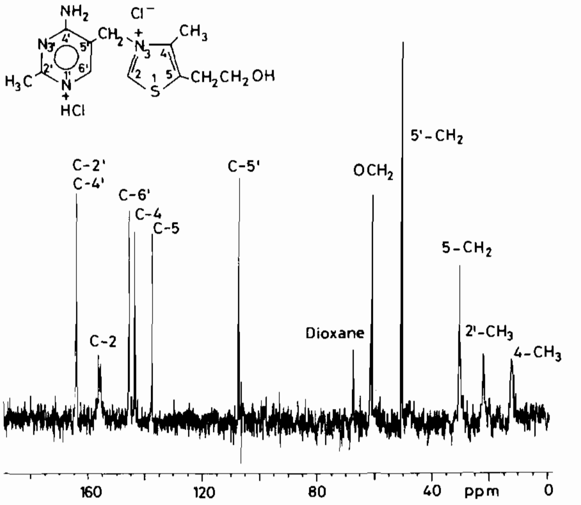

Fig. 1. ^{13}C NMR spectrum of protonated thiamine in 4 ml of water and 1 ml of D_2O with dioxane as internal reference standard.

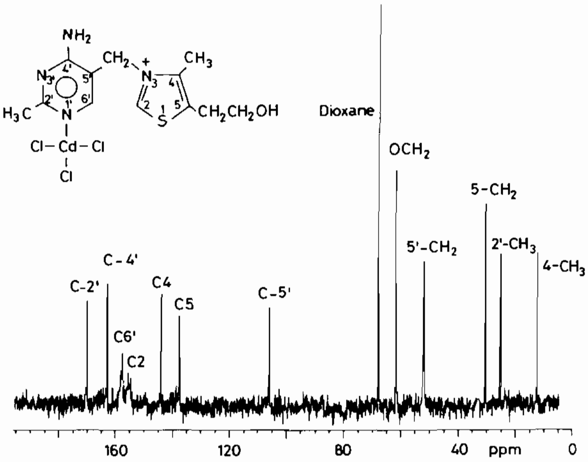

Fig. 2. ^{13}C NMR spectrum of Cd(thiamine)Cl_3 in 4 ml of water and 1 ml of D_2O with dioxane as internal reference standard.

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*Author to whom correspondence should be addressed.

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TABLE I. ^{13}C NMR Data of Protonated Thiamine and Its Cd(II) Complex, Cd(thiamine)Cl_3 in ppm (δ).

Compound	$4\text{-}CH_3$	$2'\text{-}CH_3$	$5\text{-}\alpha\text{-}CH_2$	Bridged CH_2	$5\text{-}\beta\text{-}CH_2$		
Thiamine·HCL	12.1	22.0	30.3	50.7	61.2		
Cd(Th)Cl_3	11.9	24.9	30.1	51.7	61.3		
	C-5′	C-5	C-4	C-6′	C-2	C-4′	C-2′
Thiamine·HCl	107.2	137.5	143.6	145.5	156.0	163.9	164.1
Cd(Th)Cl_3	105.6	137.1	143.6	157.3	154.8	162.6	169.9

earlier [1]. In this work, only C-6′, C-2′ and $2'\text{-}CH_3$ carbons adjacent to the coordination site experienced downfield chemical shifts while other carbons either remain essentially constant or are slightly shifted upfield. It is interesting that Theophanides *et al.* observed a downfield chemical shift of about 1.0 ppm for $2'\text{-}CH_3$ carbon compared with about 3.0 ppm for ours. Another striking observation is that C-4′ is hardly shifted (0.3 ppm) in this work as opposed to 5.3 ppm reported by Theophanides *et al.* [1]. This observation may be due to solvent effect. Although the dependence of chemical shifts on metal ions is a possibility, more NMR data on a series of thiamine metal complexes are required to prove or disprove this point.

Acknowledgements

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