The Proton Magnetic Resonance Spectrum of the Palladium(II) Schiff Base Complex Derived from Glycine and Pyruvic Acid

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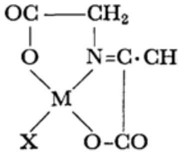
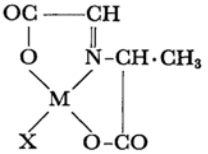
Nakao, Sakurai, and Nakahara[1] prepared a pair of copper(II) complexes of Schiff bases derived from pyruvic acid and glycine, and from glyoxylic acid and α-alanine. Although they had been belived to have different structures, A and B, in the light of many results obtained by similar preparations earlier, it was disclosed that they were



(A)



(B)

M: Cu, Pd
X: H_2O in the case of Cu
Cl in the case of Pd

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[1] Y. Nakao, K. Sakurai and A. Nakahara, This Bulletin, **38**, 687 (1965); **39**, 1471 (1966).

identical, both having the same structure, A. Since the A and B structures are different only in the relative positions of the double bond and the hydrogen atoms, the finding suggests that transamination reactions proceed *via* proton transfer. Therefore, in order to obtain deeper insight into the mechanism of transamination reactions, it is necessary to determine the behavior of the hydrogen atoms in the Schiff base complexes by some physicochemical means.

Proton magnetic resonance spectroscopy would seem to be a powerful tool for this purpose. As the copper(II) complexes were not suitable for PMR measurements, we prepared the corresponding palladium(II) complexes of Schiff bases derived from pyruvic acid and glycine, and from glyoxylic acid and α-alanine. Like the copper(II) complexes, the palladium(II) complexes proved to be identical with each other. Figure 1 shows the spectrum run in a D_2O solution. It exhibits only the signal due to the CH_3 group. This suggests that the CH_2 protons were completely exchanged for deuterium immediately after dissolution. Thus the lability of the CH_2 protons in the Schiff base complex was revealed. This kind of lability reminds us of the active methylene of the malonato chelate. Previously²⁾ we found that the signal due to the CH_2 protons in the malonato complexes dissolved in D_2O decreased in intensity with time. We interpreted the lability of the CH_2 protons as a result of the electron-withdrawing effect of the two adjacent carbonyl groups. In the Schiff base complex, the electron density of the CH_2 group may be expected to be reduced by the two unsaturated groups, $-C{=}O$ and $-N{=}C\langle$, and also through the coordination of the N atom to the metal ion. Therefore, the CH_2 protons may be expected to be highly active. Thus, it is not surprising to see the CH_2 protons more active than those in the malonato complex.

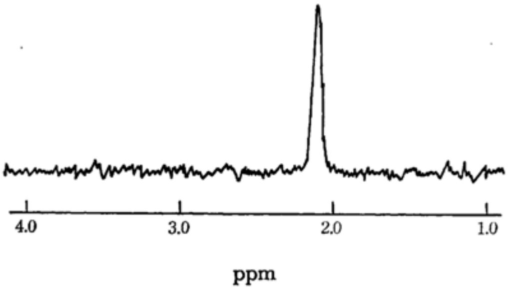

Fig. 1. The PMR spectrum of Na[Pd(pyv=gly)Cl] in D_2O.

The experimental details will be presented below.

Preparation of the Complex. Into 9 m*l* of a water : ethanol mixture (2 : 1 by volume) were stirred 0.62 g of sodium pyruvate and 0.42 g of glycine, and then 1 g of palladium chloride. After the solution had been kept at about 40°C for 2.5 hr under constant stirring, it was placed in an ice-bath. Yellow crystals thus came out. The crude product was recrystallized from a water : ethanol mixture (1 : 1 by volume). Found: C, 17.85; H, 2.53; N, 4.22%. Calcd for $\mathrm{Na[Pd(CH_3{\cdot}\underset{\substack{|\\ COO}}{C}{=}N{\cdot}CH_2{\cdot}COO)Cl]2H_2O}$: C, 17.45; H, 2.61; N, 4.08%. The same complex was obtained from glyoxylic acid and α-alanine.

NMR Measurements. The spectrum was recorded on a Varian A60 spectrometer. The chemical shift was measured relative to the sodium salt of trimethylsilyl propane sulfonic acid, taken as an internal standard.

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2) H. Yoneda and Y. Morimoto, *ibid.*, **40**, 1737 (1967).