

SHORT COMMUNICATIONS

Ethylene Proton Exchange in Cobalt(III) EDTA Complex as Evidenced by Nuclear Magnetic Resonance

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Coordinated ligands in metal complexes are under the influence of the electron-withdrawing effect of the central metal ion, and, in some complexes, some of their protons are dissociated in solution. Thus, if such complexes are dissolved in deuterium oxide, hydrogen deuterium exchange is to be observed. We noticed this kind of exchange from the finding¹⁾ that the NMR signal of the methylene protons in malonato chelates dissolved in deuterium oxide decreased in intensity with time. We have been looking for such exchange reactions by means of the NMR technique. As a result, several other exchanges were found, *i. e.* in the methylenes in trisglycinatocobalt(III)²⁾ and in the palladium complex³⁾ of glycine and pyruvic acid and in the methyl in diammine-acetylaceton-ethylenediiminecobalt(III) complex.⁴⁾

Here we wish to report an example of the exchange active ethylene group, *viz.* the ethylene group in the ethylenediaminetetraacetatocobaltate(III) complex.

Figure 1 shows the NMR spectra of the complex. Curve (a) represents the spectrum of the complex dissolved in neutral deuterium oxide. The spectrum shows a complicated pattern because the proton signals due to the ethylene and two kinds of methylenes (out-of-plane and in-plane) appear almost in the same region. Addition of a small amount of potassium carbonate to the solution caused a decrease in the intensity of the NMR signal as shown in curve (b) and (c). This is not surpris-

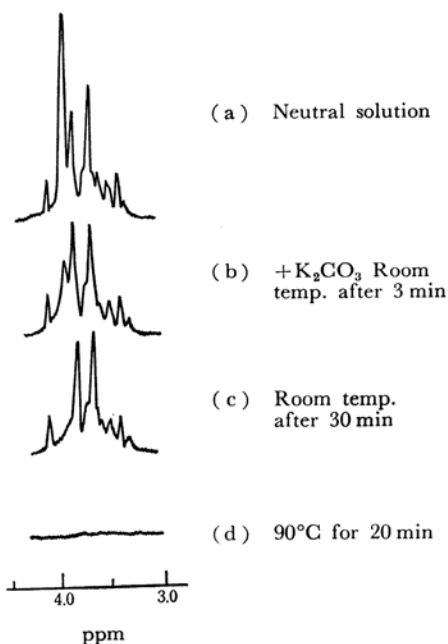


Fig. 1. The NMR spectra of Na[CoEDTA] in deuterium oxide. Sodium trimethylsilyl-propane-sulfonate was used as an internal standard.

ing because Reilley⁵⁾ already reported the hydrogen-deuterium exchange in the acetato methylenes of this complex dissolved in acidified deuterium oxide solution at elevated temperature (85–105°C). However, when the solution was kept at 90°C for 20 min, all signals due to the ethylene as well as the methylene protons completely disappeared as shown in curve (d). This means that the ethylene protons are also exchanged by deuterium at elevated temperatures.

We are now investigating the NMR spectra of other metal EDTA complexes and the results will be reported in the near future.

1) H. Yoneda and Y. Morimoto, *This Bulletin*, **40**, 1737 (1967); *Inorg. Chim. Acta*, **1**, 413 (1967).

2) unpublished.

3) H. Yoneda and Y. Morimoto, *This Bulletin*, **41**, 255 (1968).

4) H. Yoneda and Y. Morimoto, *ibid.*, **41**, 2544 (1968).

5) J. B. Terrill and C. N. Reilley, *Inorg. Chem.*, **5**, 1989 (1966).