Hydrogen-Deuterium Exchange in the Methyl Group of Diammine-bis(acetylacetone)ethylenediimine-cobalt(III) Chloride in Deuterium Oxide Solution

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We have reported several papers on the study of the proton magnetic resonance spectra of a series of cobalt(III) complexes.1) In this communication we should like to report hydrogen-deuterium exchange found in the study of the proton magnetic resonance spectra of diammine-bis(acetylacetone)-ethylenediimine-cobalt(III) chloride [Co(NH$_3$)$_2$-acac-en]Cl2) dissolved in deuterium oxide, where

acac-en =

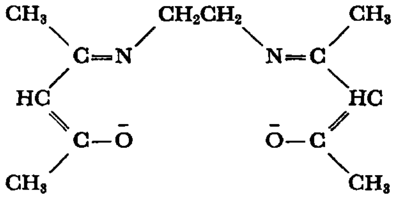

Figure 1 shows the spectra of the complex. Curve (a) represents the spectrum of the complex dissolved in neutral deuterium oxide. Putting aside a large peak due to HOD (the second peak from the left-hand side), the spectrum consists of four peaks, whose assignments can be made by considering their relative intensities. The small peak on the extreme left (I) is assigned to the CH proton, the peak in the middle (II) to the CH$_2$CH$_2$ protons, and the two peaks of equal intensities on the right (III, III') to the two kinds of CH$_3$ protons. Addition of a few drops of concentrated NaOD solution caused a slight downfield shift of all four peaks and, at the same time, a time-dependency of intensity of peaks I and III as shown in curves (b), (c), and (d). The CH peak on the extreme left decreased its intensity markedly after standing one hour and disappeared completely after 72 hr. This fact indicates that the hydrogen atom of the CH had been replaced by deuterium. This exchange can be expected, since several electrophilic substitution reactions of the CH of the acetylacetonato complexes have been reported.3) In addition to this, the inspection of curve (d) reveals another exchange. Here one of the two CH$_3$ peaks (III) is markedly smaller than the other (III'). Since the two CH$_3$ signals should have an equal intensity, this inequality can be interpreted as a result of the deuterium exchange in one of the two CH$_3$ groups. To ascertain this interpretation, the solution was kept at 100°C for 10 min to accelerate the exchange. As shown in curve (e), one of the two CH$_3$ peaks disappeared almost completely. Thus the above interpretation proved to be valid. The latter exchange is very interesting, because it provides an example where the CH$_3$ protons also can be activated by chelation.

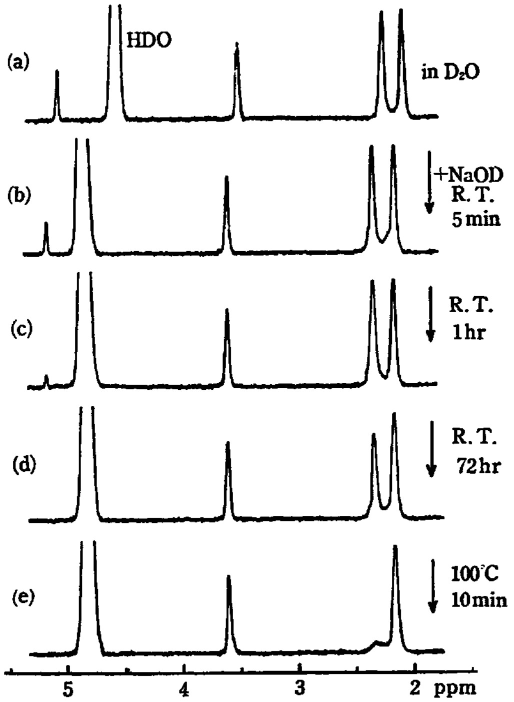

Fig. 1. The PMR spectra of [Co acacen(NH$_3$)$_2$]Cl in D$_2$O, recorded by Varian A-60 spectrometer. Tetramethylsilane was used as an external standard.

We are now working on complexes of other metal ions to see the effect of the central metal ion on the exchange. The details of the investigation will be reported elswhere.

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1) H. Yoneda and Y. Morimoto, This Bulletin, **39**, 2180 (1966); **40**, 1737 (1967); **41**, 255 (1968); *Inorg. Chim. Acta*, **1**, 413 (1967).

2) The complex was prepared according to the report by J. D. Main Smith, *J. Chem. Soc.*, **1925**, 2030. The complex was reported to be stable in acidic and basic solutions at ordinary temperatures.

3) J. P. Collman, R. A. Mose, H. Maltz and C. C. Heindel, *J. Am. Chem. Soc.*, **83**, 531 (1961); *J. Org. Chem.*, **28**, 1449 (1963); *Inorg. Chem.*, **2**, 576 (1963).