Proton Magnetic Resonance Spectrum of the Malonatobisethylenediamine Cobalt(III) Complex

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We have been interested in the study of the proton magnetic resonance of a series of cobalt(III) ammines and have written several papers on this subject.[1] In this communication we should like to report a kind of chelation effect we have found in the study of the proton magnetic resonance of [Co *mal* *en*$_2$]NO$_3$ (*mal*$=^-$OOCCH$_2$COO$^-$) dissolved in D_2O.

Figure 1 shows the spectra of the malonato complex. The upper and the lower curves represent the spectra taken, respectively, 5 and 30 min after dissolution. The broad band on the right may be assigned to the CH_2 of ethylenediamine, and the sharp signal on the left side of it, to the CH_2 of the malonato chelate ring. The broad bands on the left correspond to the two kinds of NH_2 groups in ethylenediamine. It is interesting to note that the CH_2 signal of the malonato ring decreased in intensity with time and disappeared completely upon standing overnight. This suggests that the hydrogen atoms of the malonato chelate ring are replaced by deuterium of heavy water. Such a time-change in the signal intensity was not observed in the case of sodium malonate dissolved in D_2O. In this case, even if the temperature of the solution was raised to 90°C, no appreciable decrease in the signal intensity was observed. Therefore, the time-change of the signal intensity observed in the complex can be regarded as a special effect due to chelation. This chelation effect can be understood by analogy with the process involving the active methylene of the diethyl malonate ester. That is, the electronic state of the malonato chelate may be considered to be similar to that of the malonate ester.

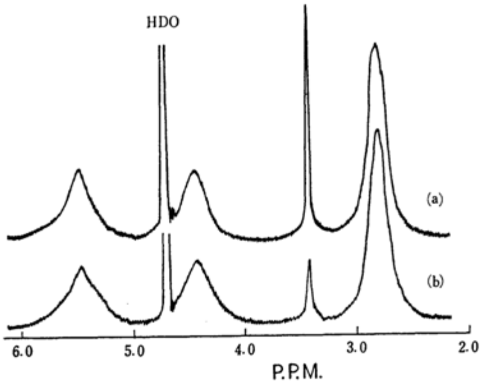

Fig. 1. The PMR spectra of [Co *mal* *en*$_2$]NO$_3$ dissolved in D_2O taken (a) 5 min and (b) 30 min after dissolution. TMS was used as an internal reference.

Further details will be reported elsewhere in the near future.

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[1] H. Yoneda and Y. Morimoto, This Bulletin, **39**, 2180 (1966) ; Proceedings of the 9th ICCC, p. 153.