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The Chelation-induced Deceleration of the Methyl Proton Exchange in the Bisacetylacetoneethylenediimine Ligand

Ichiro Takagi and Hayami Yoneda*

Department of Chemistry, Faculty of Education, Wakayama University, Masagocho, Wakayama 640

**Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima 730*

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Organic ligands in chelate compounds are subject to the influence of the electron-withdrawing effect of a central metal ion, and, as a result, proton dissociation from the ligand is more or less facilitated. Therefore, hydrogen-deuterium exchange can be observed in some complexes when they are dissolved in deuterium oxide. This kind of exchange can easily be detected and followed by measuring the intensity decrease in the PMR signal of the coordinated ligand. We have found several such examples, *i.e.*, in the methylene of the malonato[1] and glycinato[2] cobalt(III) complexes, in the ethylene of the EDTA cobalt(III) complex,[3] and in the methyl of dimethylglyoximatocobalt(III) complexes.[4] In all these cases, the free ligand itself does not show such an exchange, and chelation is considered to accelerate it.

Here we would like to report another type of chelation effect, one which slows down the rate of proton exchange. The complexes studied are four kinds of bisacetylacetoneethylenediiminecobalt(III) with the formula of $[CoX_2acac\text{-}en]^{n+}$, where X is NO_2^-, pyridine, NH_3, and CH_3NH_2. These complexes were dissolved in a 2% NaOD deuterium oxide solution, and the PMR spectra were measured at 60 °C at appropriate time intervals. For comparison, the time change in the PMR spectrum of the free ligand itself was also recorded under the same conditions. Figure 1 shows the spectra of $[Co(NH_3)_2acac\text{-}en]NO_3$ measured (a) immediately and (b) 240 min after dissolution. A comparison of

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

[2] H. Yoneda and Y. Morimoto, *Kagaku no Ryoiki*, **22**, 826 (1968).

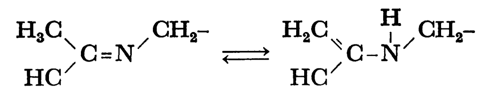
[3] H. Yoneda and Y. Morimoto, This Bulletin, **42**, 1160 (1969).

[4] H. Yoneda, I. Takagi, and Y. Morimoto, *ibid.*, **44**, 2863 (1971).

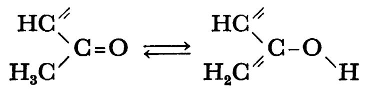
the two spectra, (a) and (b), reveals that the H–D exchange occurred at two sites of the ligand, namely, at the vinyl and at one of the two methyls. At present we have no unambiguous evidence with which to decide which methyl of the two (one adjacent to C=N and the other adjacent to C–O) is exchange-active. However, the exchange-rate constant in the methyl can easily be determined from the slope in Fig. 2.

The rate constants obtained for the free ligand and for the four complexes (10^{-3} min^{-1} unit) are 57.7 (free ligand), 6.6 (CH_3NH_2), 2.9 (NH_3), 1.6 (pyridine), and 0.7 (NO_2^-).

Here it should be noted that the exchange rate for the free ligand is ten times as large or larger than those for the complexes. This large exchange rate in the methyl of the free ligand can be understood by means of the following tautomeric mechanism:



or



This kind of tautomerism is depressed by chelation, which results in a decrease in the exchange rate in the complexes. In other words, chelation fixes the planar atomic arrangement of the acetylacetone group and gives it a pseudoaromatic character, which then serves to reduce the contribution of the electronic state favorable for the above-mentioned tautomerism. The decreasing order of the rate constants for the four complexes is; $CH_3NH_2 > NH_3 > \text{pyridine} > NO_2^-$ and corresponds to the increasing order of the degree of the charge neutralization of the metal ion caused by the ligand, X. Therefore, this trend suggests that the electron-withdrawing effect of the metal ion is the only driving force for the proton exchange in the complexes.

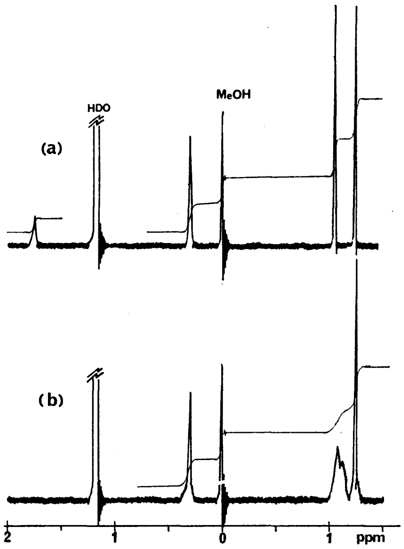


Fig. 1. The PMR spectra of $[Co(NH_3)_2\text{acac-en}]NO_3$ in 2% NaOD–D_2O solution at 60 °C recorded (a) immediately and (b) 240 min after dissolution.

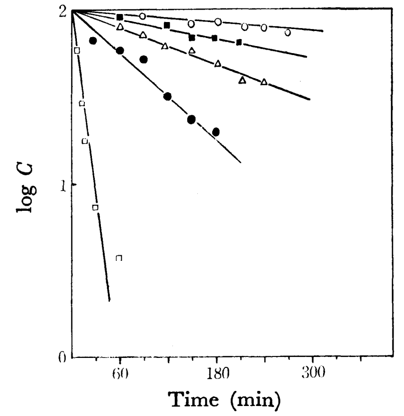


Fig. 2. Plots of the methyl signal intensity of the bisacetylacetoneethylenediimine ligand against time (60 °C).
□: the free ligand, ●: $[Co(CH_3NH_2)_2\text{acac-en}]^+$,
△: $[Co(NH_3)_2\text{acac-en}]^+$, ■: $[Co(py)_2\text{acac-en}]^+$,
○: $[Co(NO_2)_2\text{acac-en}]^-$.

Experimental

Materials. The $[CoX_2\text{acac-en}]ClO_4$ ($X = CH_3NH_2$, NH_3, and pyridine) and $Na[Co(NO_2)_2\text{acac-en}]$ complexes were prepared according to the method reported by Fujii.[5)]

NMR Measurements. The spectra were recorded in a 2% NaOD deuterium oxide solution on a Jeol JNM-C-60HL spectrometer. Methanol was added to the solution as an internal standard for the chemical shift and the intensity.

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5) Y. Fujii A. Osawa, Y. Furukawa, F. Ebina, and S. Takahashi, This Bulletin, **45**, 2459 (1972).