# Hydrogen-Deuterium Exchange in the Methyl Group of Four Bisdimethylglyoximatocobalt(III) Complexes

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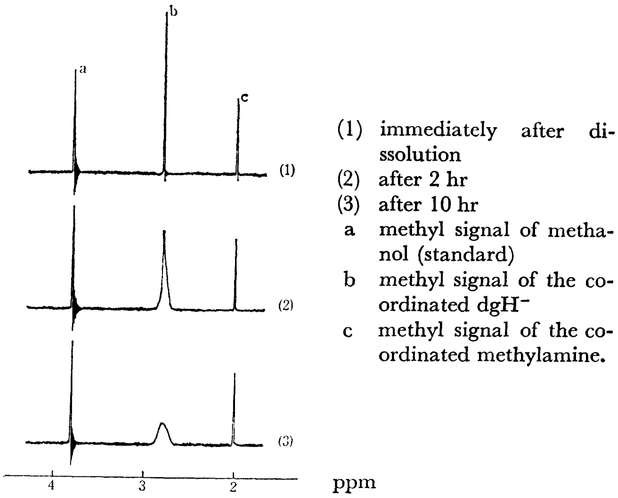
Organic ligands in chelate compounds are under the influence of the electron-withdrawing effect of a central metal ion, and as a result, proton dissociation from the ligands is more or less facilitated. Thus, hydrogen-deuterium exchange is to be observed in some complexes, when they are dissolved in deuterium oxide. We noticed this kind of exchange from the fact that the intensity of the PMR signal of methylene in malonato chelates dissolved in deuterium oxide decreased with time.[1] Thus, the NMR technique proved to be useful for the study of proton exchange reactions. Several other examples have been found, *i.e.* in the methylene of the glycinatocobalt(III) complex,[2] in the methylene of the palladium Schiff base complex of glycine and pyruvic acid,[3] in the methyl of the acetylacetoneethylenediiminecobalt(III) complex[4] and in the ethylene of the EDTA-cobalt(III) complex.[5]

We would like to report a similar hydrogen-deuterium exchange in the methyl group of a series of bisdimethylglyoximatocobalt(III) complexes of the formula $[CoX_2(dgH)_2]^{+ \text{or} -}$ in which X is $CN^-$, $NO_2^-$, $NH_3$, or $CH_3NH_2$. It should be noticed that the exchange rate is dependent on the kind of the axial ligand X.



(1) immediately after dissolution
(2) after 2 hr
(3) after 10 hr
a methyl signal of methanol (standard)
b methyl signal of the coordinated $dgH^-$
c methyl signal of the coordinated methylamine.

Fig. 1. The PMR spectra of $[Co(CH_3NH_2)_2(dgH)_2]Cl$ in 2% NaOD-$D_2O$ solution, measured at 20°C.

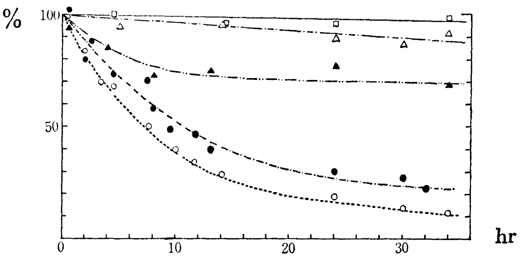


Fig. 2. Plots of the methyl signal intensity of the dimethylglyoximato ligand against time.

$dgH^-$ □, ————
$Na[Co(CN)_2(dgH)_2]$ △, —·—·—·—
$Na[Co(NO_2)_2(dgH)_2]$ ▲, —··—··—
$[Co(NH_3)_2(dgH)_2]Cl$ ●, —·—·—·—
$[Co(CH_3NH_2)_2(dgH)_2]Cl$ ○, ··········

Figure 1 shows the time change of the PMR spectrum of $[Co(CH_3NH_2)_2(dgH)_2]Cl$ in 2% NaOD deuterium oxide solution at 20°C. The methyl signal of the dimethylglyoximato ligand lies in the middle of the spectrum and shows the intensity decrease and line-broadening with time (Fig. 1, (1), (2), and (3)). This is clearly due to the hydrogen-deuterium exchange

$$-CH_3 \longrightarrow -CH_2D \longrightarrow -CHD_2 \longrightarrow -CD_3$$

The line-broadening is due to the spin-spin coupling between H and D in the intermediates $CH_2D$ and $CHD_2$.

Thus, the exchange reaction can be followed as the intensity decrease of the methyl signal of the coordinated ligand. The result obtained for the four complexes is shown in Fig. 2. We see that the exchange rate for the free ligand is negligibly small, compared with that of any one of the four complexes tested, and we can conclude that the activation of ligand protons is induced by chelation. It should be pointed out that the exchange in the cyano complex goes very slowly while the exchange in the methylamine complex proceeds fairly fast. Thus, the exchange rate is in the order $CH_3NH_2 > NH_3 > NO_2^- > CN^-$. The half-value periods for these complexes are 7.5 hr for the methylamine, 11 hr for the ammonia, 200 hr for the cyano complexes and more than 1000 hr for the free ligand. The half-value period for the nitro complex lies between those of the ammonia and cyano complexes, but decomposition of the complex prevented determination of the exact value. This exchange rate order is just the reverse of the order of positions of these ligand X in the spectrochemical series. This trend can be interpreted in the following way. Since the activation of ligand protons is induced by the electron-withdrawing effect of a central metal ion, the less positive the effective charge of the metal ion, the smaller the exchange rate of the ligand protons. The smallest exchange rate for the cyano complex is the reflection of the almost complete neutralization of the positive charge of the central metal ion which is caused by the strong coordination of the cyano groups.

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

2) unpublished.

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

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

5) H. Yoneda and Y. Morimoto, *ibid.*, **42**, 1160 (1969).