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HYDROXIDE ADDITION TO THE COBALT(III) MIXED LIGAND COMPLEX, (1,1,1,5,5,5-HEXAFLUOROACETYLACETONATO)BIS(ETHYLENEDIAMINE)COBALT(III) PERCHLORATE

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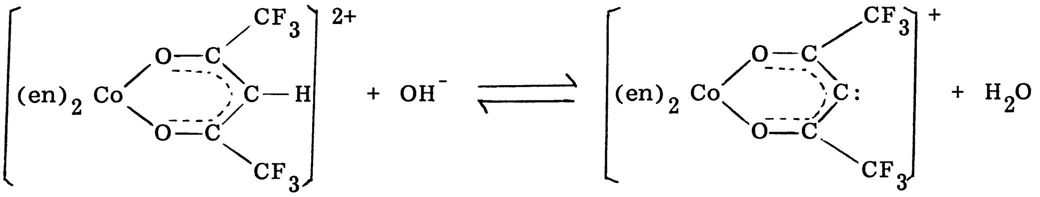
NMR studies revealed that the reaction of the title complex, $[Co(hfac)(en)_2](ClO_4)_2$ with OH^- in an aqeous solution is the addition of OH^- to the carbonyl carbon of coordinated hfac.

β-Diketonates are well-known chelating agents which form characteristic complexes with various metal ions, e.g., those with high volatility or solubility in non-polar solvents.1) Many works have been done on the ligand reactions of these complexes, for example, halogenation as a substitution reaction of the methine proton.2) As to the complexes of 1,1,1,5,5,5-hexafluoroacetylacetonate(hfac), however, no such reaction has been reported.

A few years ago, one of us(K. K.) synthesized the title complex, and found that the color of its aqeous solution changes reversibly from orange to pink and vice versa by the addition of NaOH and HCl. This change was explained in terms of an acid-base equilibrium, involving the deprotonation of hfac, on the basis of spectrophotometric data(Scheme 1).4)



(Scheme 1)

We reinvestigated this system by means of NMR , and compared the obtained data with those of $[Co(acac)(en)_2](ClO_4)_2$ which does not show such a color change.

Figure 1 shows some typical ^1H-NMR spectra. In D_2O, the methine signal appears at 6.63 ppm and 5.74 ppm (internal reference: DSS), respectively, in the two systems, $[Co(hfac)(en)_2](ClO_4)_2$ and $[Co(acac)(en)_2](ClO_4)_2$. When these solutions were made basic with NaOD, the signal of the former shifted remarkably to higher field (5.09 ppm), but that of the latter remained nearly unchanged. When these basic solutions were made acidic again with DCl, the signal of the former returned exactly to its original position without losing the intensity, whereas that of the latter disappeared completely. These observations indicate, rather unexpectedly, that the exchange of the methine proton does not occur for the hfac system under any pH conditions, whereas it occurs in the acac system in acidic solutions.

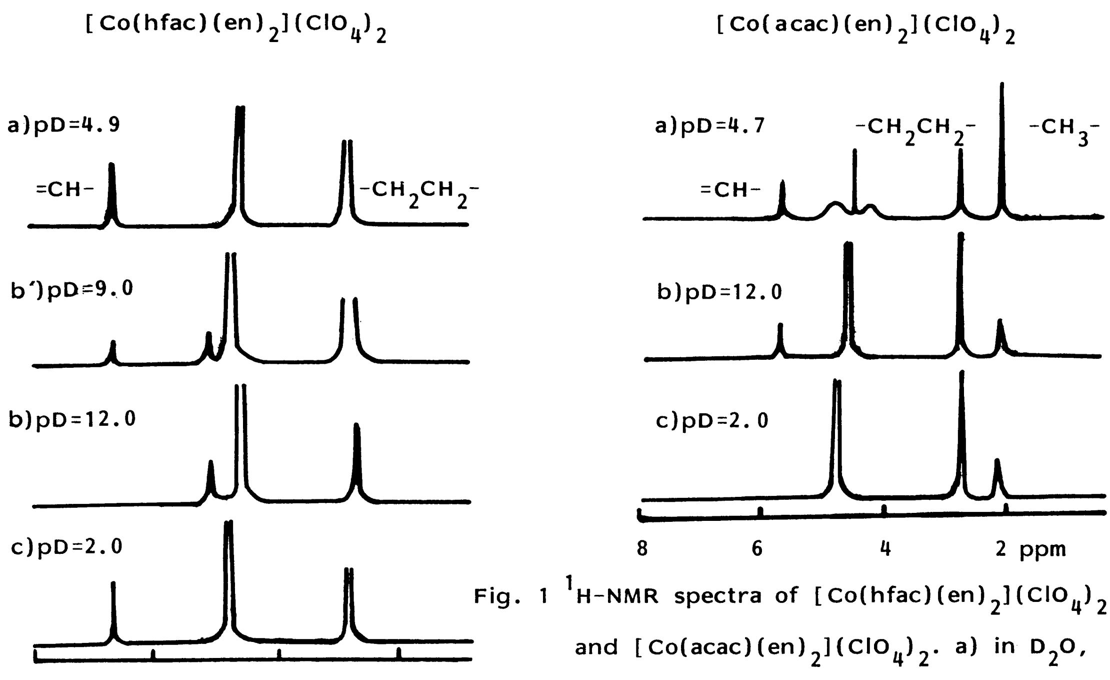


Fig. 1 ^{1}H-NMR spectra of $[Co(hfac)(en)_2](ClO_4)_2$ and $[Co(acac)(en)_2](ClO_4)_2$. a) in D_2O, b) and b′) in D_2O+NaOD, c) solution b)+DCl.

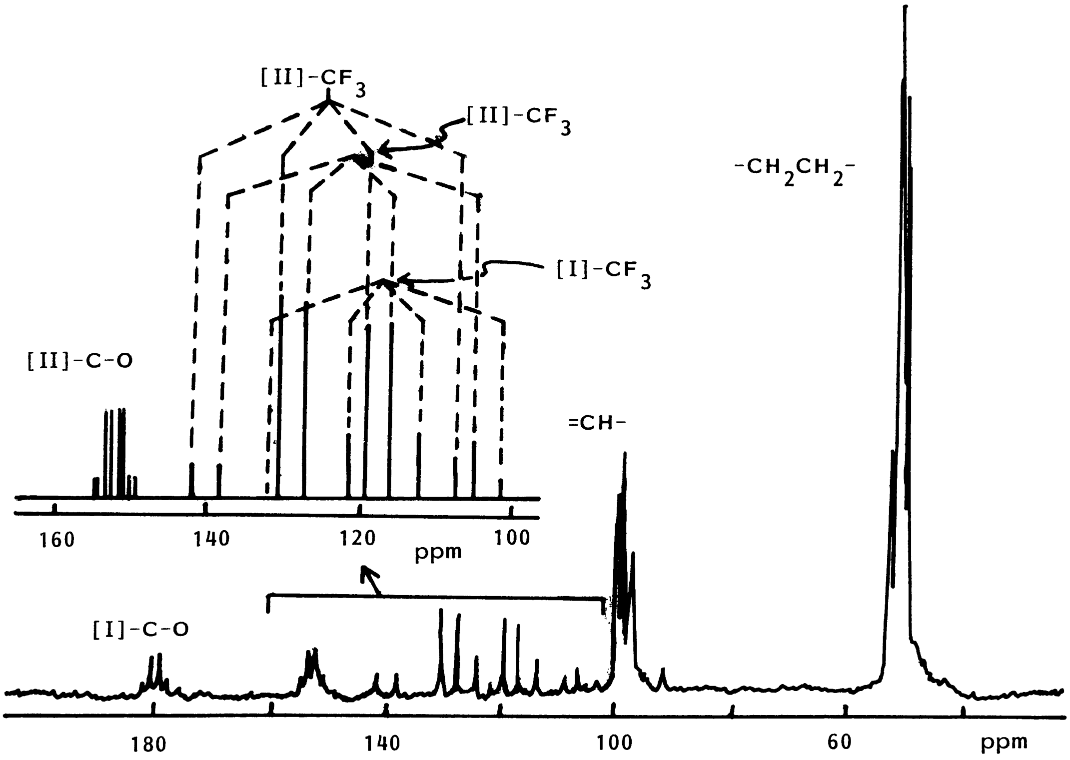
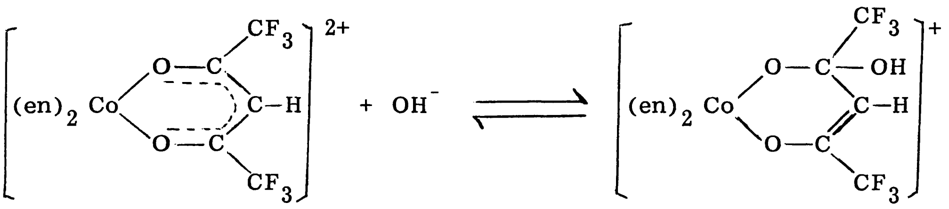


Fig. 2 ^{13}C-NMR spectrum of $[Co(hfac)(en)_2](ClO_4)_2$ in basic medium (pD=9.0). [I]=acidic form, and [II]=basic form.

Figure 2 shows a representative ^{13}C-NMR spectrum of $[Co(hfac)(en)_2]^{2+}$ in basic solution, prepared by adding NaOD to its aqueous solution under CO_2-free condition. The spectrum is complicated owing to the co-existence of a small amount of the original complex which is called "acidic form", but by careful comparison of the data with those obtained in neutral condition, we can eliminate the peaks of the acidic form, and obtain the spectrum of the pure "basic form" complex.*
A part of the spectrum analyzed in this way is shown in a simplified and expanded form in the same figure. We can easily see that two CF_3 and two C-O groups are, respectively, not equivalent in the basic form.

These NMR data indicate that the scheme 1 is not the case, i.e., that the color change of the hfac complex is not due to the deprotonation of coordinated hfac. The alternative view, which is consistent with all these data, seems to be the scheme 2:



(Scheme 2)

By means of this scheme, we can explain the shift of the hfac-methine signal of the basic form to higher field (as compared with that of the acidic form) in terms of the localization of C=C bond. As to the ^{13}C-NMR results, the chemical shifts of the two carbonyl carbons of the basic form are quite similar in magnitude, and both are shifted to higher field as compared with those of the acidic form. According to this scheme, one of these carbons in the basic form is a sp^3 carbon, which will show NMR signals similar to the sugar carbons combined with two O or OH atoms,$^{3)}$ and another is a sp^2 carbon, which is more ethylenic, and will show NMR signals at higher field than the carbonyl carbons in the acidic form. The similarity in the chemical shifts of these two carbons in the basic form is thus quite conceivable. Another possible explanation, involving the coordinative attack of OH^- to Co(III) and partial destruction of the chelate structure (equation 1),

$$[Co(hfac)(en)_2]^{2+} + OH^- \rightleftharpoons [Co(hfac')(en)_2]^+ \text{ (hfac'=monodentate hfac)} \qquad (1)$$

is improbable because the optical activity of the complex resolved, $(+)_D$-$[Co(hfac)(en)_2]^{2+}$remains unchanged when its solution is made basic and then acidified again,$^{4)}$ and the NMR data of the basic form cannot be explained well with the assumption of monodentate hfac.

The scheme 2 is also compatible with the disappearance of the strong UV absorption of the hfac complex at about 28000 cm^{-1} in basic solution, which may be taken as an indication for a drastic change in the degree of delocalization of the π-electron system in the complex.

Why does the hfac behave as a Lewis acid as in scheme 2, and not as a Brönsted acid as in scheme 1? This is probably because the electron density around the methine carbon in the hfac

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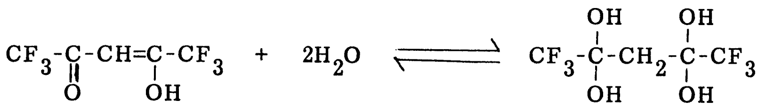
* Unfortunately we could not obtain the spectrum of the pure basic form at higher pD, because of the gradual decomposition during the long time of ^{13}C-NMR measurement.

complex is quite low, owing to the electron-withdrawing effect of the two CF_3 groups. The electrophilic attack such as the $H \rightleftharpoons D$ exchange or halogenation is thus not likely to occur, in contrast to the acac system where such attacks are quite common. The interaction of the hfac complex with alkalis occurs thus most probably through the capture of OH^- by one of the carbonyl carbons.

In this connection, it is interesting to note the finding of Sato and his co-workers[5)] that similar nucleophilic attack to the carbonyl groups occurs when Hhfac reacts with water to form the dihydrate according to the equation:[5)]



$$\mathrm{CF_3-\underset{\underset{O}{\|}}{C}-CH=\underset{\underset{OH}{|}}{C}-CF_3 + 2H_2O \rightleftharpoons CF_3-\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2-\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{C}}-CF_3} \qquad (2)$$

The study of Ebina and his co-workers,[6)] who found that the ligand in an antimony complex of 1,1,1-trifluoroacetylacetonate, $(p\text{-}ClC_6H_4)_3Sb(CF_3\text{-}(O^-)_2\text{-}CH_2\text{-}CO\text{-}CH_3)$, is in a situation similar to the basic form of the present study, is also interesting; In their case, however, after the addition of OH^- to the carbonyl carbon and H^+ to the methine carbon a proton is released from the OH group and the resulting $-O^-$ acts also as a coordinating atom. These findings also seem to be in support of the proposed scheme.

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