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HEXAFLUOROACETYLACETONATOBIS(ETHYLENEDIAMINE)COBALT(III) PERCHLORATE, REVERSIBLE CHANGES OF ITS ABSORPTION AND ROTATION WITH ACID AND BASE

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Hexafluoroacetylacetonatobis(ethylenediamine)cobalt(III) perchlorate, $[Co(hfac)(en)_2](ClO_4)_2$ has been prepared and resolved. It has been found that reversible changes in absorption and rotation occur with the variation of the pH of the solution. It has been considered from the facts that the deprotonation of the methylidyne group in hfac may be accompanied with a variation in the electronic state and the steric distribution of the electron density in the chelate ring.

It is well-known that hexafluoroacetylacetone (abbreviated as Hhfac in this paper) produces $[M(II)(hfac)_2]$ and $[M(III)(hfac)_3]$ type complexes. Because of their volatile character, these complexes attracted attention from the standpoints of the gas chromatography of metals and laser source materials, and subsequently have been extensively investigated. However, mixed ligand complexes with this ligand have hardly been studied so far.[1] In this paper, the preparation and resolution of hexafluoroacetylacetonatobis(ethylenediamine)cobalt(III) perchlorate, $[Co(hfac)(en)_2](ClO_4)_2$, are described and its big and reversible changes in absorption and rotation which occur between acidic and basic solutions are reported.

Preparation and Resolution of $[Co(hfac)(en)_2](ClO_4)_2$.* In 5 ml of water, 3.4 g of $[CoCO_3(en)_2]ClO_4$ was dissolved by the addition of 3.5 ml of 6M $HClO_4$. Into a solution which contained 0.5 g of NaOH in 5 ml of water, 2.1 g of Hhfac was added. The two solutions were combined and the mixture amounted about 20 ml due to the addition of the washings. It was heated at 45°C for 30 min with stirring, and then was concentrated at this temperature to about 5 ml with the aid of air stream onto the surface. A large amount of deep orange crystals came out by cooling. The crystals were collected on a filter and then extracted with 10 ml of ethanol. Thus, a recrystallized product was obtained by the spontaneous evaporation of the solvent to some extent. It was collected and washed with ethanol-ether(50%) mixture and then with ether. Yield, 4.5 g. Found: C, 18.44, H, 2.96, N, 9.84%. Calcd for $[Co(hfac)(en)_2](ClO_4)_2$ = $CoC_9H_{17}O_{10}N_4Cl_2F_6$(585.08): C, 18.48, H, 2.93, N, 9.58%.

The deposit of this material from an aqueous medium is very soluble in methanol, ethanol, and acetone, especially when it is wet. Therefore, it is unable to wash with these solvents. The deposit from a medium composed mainly of ethanol is washable with ethanol-ether mixture, as has been described above, without much dissolution of the product. This property was utilized in the resolution of the complex, too.

In 30 ml of water, 2.9 g of $[Co(hfac)(en)_2](ClO_4)_2$ was dissolved. In 20 ml of water, 1.3 g of the so-called sodium $(+)_D$-arsinyl tartrate was dissolved. The two solutions were combined and the mixture was kept in a refrigerator overnight. It turned into a muddy state due to the deposition of a large amount of a diastereoisomeric salt which was considered to be $(+)_D$-$[Co(hfac)(en)_2][(+)_D$-$As_2(C_4H_2O_6)_2]$. The deposit was collected and washed with a small amount of cold water, ethanol-ether(50%) mixture, and then with ether. Yield, 1.0 g.

In 50 ml of ethanol, 1.0 g of the diastereoisomeric salt was suspended and 5 ml of aqueous 2M $NaClO_4$ was added. The mixture was vigorously stirred at 45°C until the solid phase turned completely into white (~ 1 hr). The solid was removed by filtration, and the orange filtrate was concentrated to dryness at 45°C. Deep orange crystals, which came out with a small amount of the white material, were extracted with 10 ml of ethanol, and a recrystallized product was obtained by the spontaneous evaporation of the solvent from the extract. The crystals were washed with ethanol-ether(50%) mixture and then with ether. Yield, 0.5 g. The purity of the product was confirmed by the coincidence of the absorption with that of the unresolved complex.

Absorption Spectrum and Its Variation with Acid and Base. The absorption spectra of the complex and of $[Co(acac)(en)_2](ClO_4)_2$ were measured with 0.005 molar solutions for the visible region and with 0.0005 and 0.00005 molar solutions for the UV resion. Figure 1 shows the absorption curves of the complex in water and in a basic (0.1M NaOH) solution, as well as that of the acac-complex. The absorption curve of the hfac-complex in acidic solutions coincides with that in water, and the spectrum of the acac-complex in a basic (0.1M NaOH) solution was confirmed to be identical with that in water.

Several interesting points may be noticed in the spectra. First, the absorption maximum of the 1st band lies at a higher wave number than that of the acac-complex. Therefore, it has been found that hfac ranks higher than acac in the spectrochemical series. Second, the specific absorption at 28,600 cm^{-1}, which corresponds apparently to the band at 30,700 cm^{-1} of the acac-complex, may be assigned to the $\pi^* \leftarrow t_{2g}$ transition as in the acac-complex.[2] It is interesting to note that in the basic solution not only the 1st band shifts to a considerably lower wave number, but also the specific band virtually disappeared. Furthermore, when the basic solution is acidified by the addition of $HClO_4$, the spectrum returns reversibly to the original one. The visual color in basic solutions is red-violet, thus the color change is just like a reverse of methyl orange.

The mechanism of this phenomenon may be considered like acid-base indicators: as a result of deprotonation of the central methylidyne group in hfac, the original delocalized π electrons in the chelate ring change their state to a localized form such as;

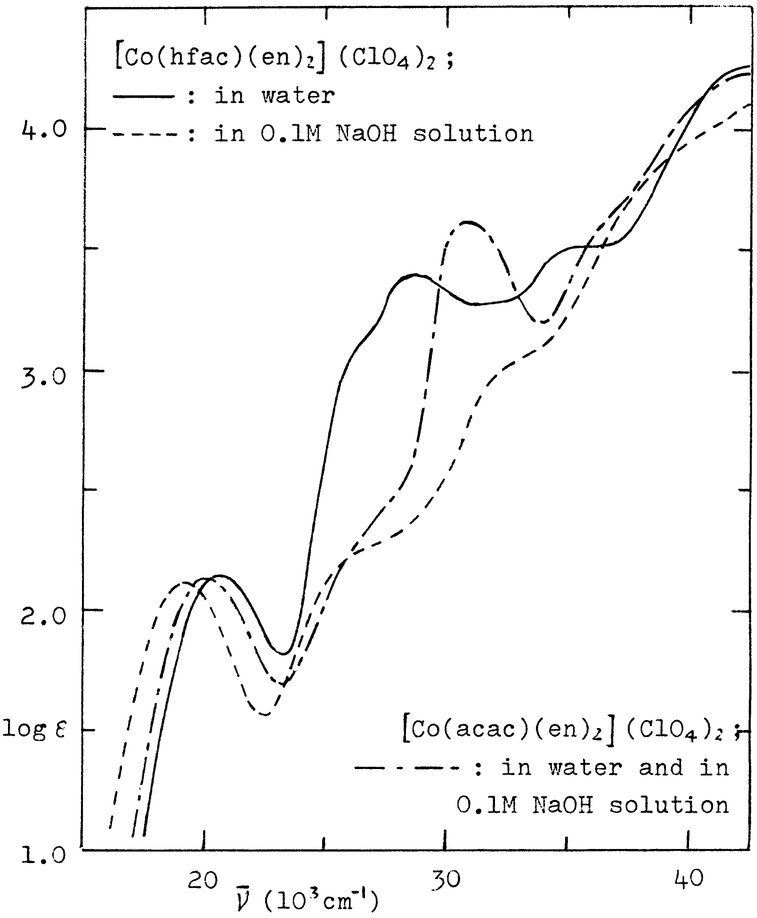
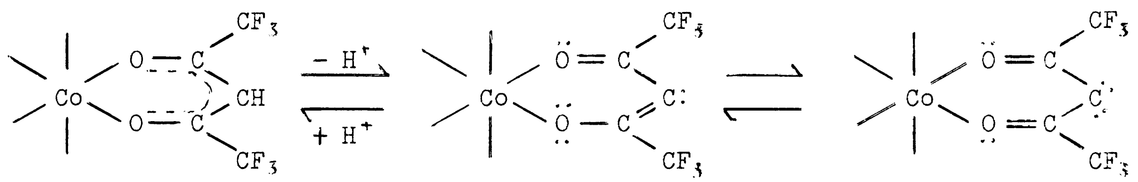


Fig. 1 Absorption spectra of $[Co(hfac)(en)_2](ClO_4)_2$ in water and in a basic solution.



(The electrons located, in the above formula, on the central carbon atom may be, in reality, strongly attracted by fluorine atoms.)

Rotation and Its Variation with Acid and Base. The molar rotations of the resolved complex, $(+)_D$-$[Co(hfac)(en)_2](ClO_4)_2$, in water and in a basic (0.1M NaOH) solution are listed in Table 1. The rotations of $(+)_D$-$[Co(acac)(en)_2](ClO_4)_2$[3] are also shown for comparison. The rotational character of the complex is essentially similar with that of the acac-complex. Therefore, the $(+)_D$-isomer may be assigned to have the Λ-configuration.[4]

Table 1. Molar Rotations of (+)$_D$-[Co(hfac or acac)(en)$_2$](ClO$_4$)$_2$

	$[M]_{589}$	$[M]_{577}$	$[M]_{546}$	$[M]_{435}$	$[M]_{405}$
(+)$_D$-[Co(hfac)(en)$_2$](ClO$_4$)$_2$					
in the neutral solution	+ 2,080°	+ 2,560°	+ 3,400°	- 12,770°	-14,230°
in the basic solution	+ 1,890°	+ 1,310°	- 2,130°	- 3,870°	- 4,250°
(+)$_D$-[Co(acac)(en)$_2$](ClO$_4$)$_2$					
in the neutral solution	+ 2,280°	+ 2,900°	+ 3,200°	- 11,500°	-11,800°

It is interesting to note that the rotations also change greatly their values in basic solutions and return reversibly to their original values by acidifying with HClO$_4$. Such big changes in rotation may not be explained by the localization of the π electrons alone, since the change in total electron density, which affects the rotations, may be small. It may be more reasonable to assume that the deprotonation of the methylidyne group in hfac is also accompanied with a variation in the steric distribution of the total electron density with some transformation of the chelate ring.

References and Footnote:

* The preparative works should be performed in a draft chamber and with gum gloves, otherwise the vapor of Hhfac may hurt skin and cause eruption.

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