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Synthesis and Identification of a Series of Hexafluoroacetylacetonato Complexes of Cobalt(III). Spectroscopic Analyses of the Reversible Addition of Hydroxide to the Coordinated Ligand in Aqueous Solution

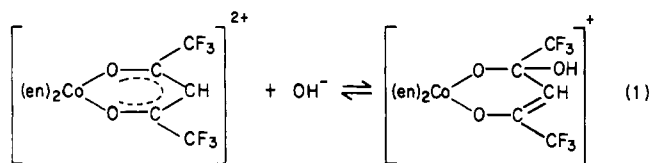
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A series of hexafluoroacetylacetonato (hfac) complexes of Co(III) were synthesized and identified. These include the complexes $[\text{Co}(\text{NH}_3)_4(\text{hfac})](\text{ClO}_4)_2$, α - and β - $[\text{Co}(\text{trien})(\text{hfac})](\text{ClO}_4)_2$, *mer(N)*- and *fac(N)*- $[\text{Co}(\text{i-dtma})(\text{hfac})]\text{ClO}_4$, and α - and β - $[\text{Co}(\text{edda})(\text{hfac})](\text{ClO}_4)_2$ (trien = triethylenetetramine, i-dtma = 4-diethylenetriaminemonoacetate, edda = ethylenediaminediacetate). All these complexes exhibit a unique reaction with base during which addition of OH^- to the coordinated hfac ligand occurs. This reaction is reversible and was studied spectroscopically with use of UV-visible and ^1H , ^{13}C , and ^{19}F NMR techniques. The NMR spectra reveal that different isomeric forms of the reaction product are produced depending on the nature of the nonparticipating ligand.

Introduction

So far only one hexafluoroacetylacetonato (hfac) complex of Co(III), viz. $\text{Co}(\text{en})_2(\text{hfac})^{2+}$ where en = ethylenediamine, has been reported to exhibit a rather remarkable change in color when base is added to an aqueous solution of this complex. Although initial studies³ suggested that deprotonation of the methine center on the coordinated hfac ligand could account for this observation, a later study⁴ provided ^1H and ^{13}C NMR evidence in favor of the addition of OH^- to the coordinated ligand, viz.



It was found⁴ that the signal for the methine proton in D_2O between 6 and 7 ppm disappeared on the addition of base and a new signal appeared at higher field between 5 and 5.5 ppm. The process could be reversed upon addition of acid, indicating that H/D exchange did not occur for this group. The addition of OH^- to the adjacent carbon atom was suggested to account for the observed shift in alkaline medium.

We recently found that ^{19}F NMR measurements could be employed with even greater success in the elucidation of such reaction processes. In the meantime we have synthesized and identified an additional seven hfac complexes of Co(III) that all exhibit a reversible reaction with OH^- similar to that outlined above. Details on the synthetic procedures and the spectroscopic findings using UV-visible and ^1H , ^{13}C , and ^{19}F NMR techniques are reported in this paper.

Experimental Section

Materials. The following complexes were prepared in a similar way as described³ for $[\text{Co}(\text{en})_2(\text{hfac})](\text{ClO}_4)_2$ by using the corresponding carbonate complex^{5,6} as starting material:⁷ $[\text{Co}(\text{NH}_3)_4(\text{hfac})]\text{ClO}_4$, α - $[\text{Co}(\text{trien})(\text{hfac})](\text{ClO}_4)_2$, and β - $[\text{Co}(\text{trien})(\text{hfac})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (trien = triethylenetetramine). *fac(N)*- $[\text{Co}(\text{i-dtma})(\text{hfac})]\text{ClO}_4$ (i-dtma = 4-diethylenetriaminemonoacetate) was prepared as follows: 3.7 g of *mer(N)*- $[\text{Co}(\text{i-dtma})(\text{H}_2\text{O})\text{Cl}]\text{ClO}_4$ ⁸ was suspended in 20 mL of water,

and 2.0 g of AgClO_4 was added. The suspension was heated on a water bath for 30 min, during which dissolution and aquation of the complex occurred. After removal of the AgCl precipitate by filtration, 5 mL of 6 M HClO_4 was added to the deep red solution, and the latter was evaporated almost to dryness on a water bath. An air stream was used to assist the evaporation, and in case no crystalline product resulted, a few milliliters of water was added and the evaporation procedure was repeated several times. Finally the *fac(N)*- $[\text{Co}(\text{i-dtma})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ product crystallized as deep red crystals, which were collected on a glass filter and washed with a 20% ethanol-80% ether mixture, followed by ether. The yield of the diaquo complex (4.2 g) is almost quantitative. Caution should be taken to prevent the use of an excess of AgClO_4 , since this complicates the crystallization process. Conversion to the hfac complex was accomplished by treating 4.7 g of the diaquo complex with 2.1 g of Hhfac and 0.5 g of NaOH in 20 mL of water similar to that described for the corresponding bis(ethylenediamine) complex.³

mer(N)- $[\text{Co}(\text{i-dtma})(\text{hfac})]\text{ClO}_4$ was prepared by mixing 4.7 g of *fac(N)*- $[\text{Co}(\text{i-dtma})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$, 2.1 g of Hhfac, 0.5 g of NaOH, and 0.1 g of active charcoal in 20 mL of water. This mixture was heated on a water bath for 30 min under constant stirring, after which the charcoal was filtered off, 1 mL of 6 M HClO_4 was added, and the solution was slowly evaporated to a final volume of 3 mL. The early deposits (up to a volume of 5 mL), which were orange and clearly differed from the *fac(N)* isomer, were collected and recrystallized from 20 mL of warm water by the addition of a few drops of 6 M HClO_4 . The final product was washed with a 20% ethanol-80% ether mixture, followed by ether. The yield amounted to 2.5 g. The later deposits during continued evaporation turned out to be a mixture of both isomers.

The α - and β - $[\text{Co}(\text{edda})(\text{hfac})]$ (edda = ethylenediaminediacetate) complexes were prepared in the following way: 1.7 g of α - $[\text{Co}(\text{edda})(\text{H}_2\text{O})_2]\text{ClO}_4$ ⁹ was mixed with 1 g of Hhfac and 0.2 g of NaOH in 30 mL of water and stirred for 1 h at 70 °C. After cooling, the deposited crystals were collected on a filter and washed with ethanol and ether. A concentrated solution of this product was placed on an ion-exchange column (Dowex 50W-X8, H^+ form, 200-400 mesh) and eluted with water. The first red-violet band was concentrated under reduced pressure at 60 °C and the resulting precipitate recrystallized from methanol. Spectroscopic analysis (see further discussion) proved this species to be the α isomer. The second red-brown band was concentrated in a similar way, and the produced precipitate was recrystallized from methanol. Spectroscopic analysis confirmed this to be the β isomer.

The isolated complexes were subjected to chemical analyses, the results of which are shown in Table I. Chemicals of analytical reagent grade and doubly distilled water were used in the preparation of all solutions. Ionic strength was adjusted with NaClO_4 .

Spectroscopic Measurements. UV-visible absorption spectra were recorded on Zeiss DMR 10, Perkin-Elmer 555, Hitachi EPS-3T, and Nihon Bunko UVIDEK 505 spectrophotometers. All the hfac complexes exhibit characteristic spectral changes as a function of pH, which can be employed to determine the equilibrium constants spectrophotometrically. Such data can also be obtained from conventional pH titrations.¹⁰ pH measurements were performed on Hitachi-Horiba F-7DE and Radiometer PHM 64 instruments.

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(7) All preparative work should be performed in a fume cupboard to avoid contact with Hhfac fumes. *Warning!* Care should be taken since perchlorate salts are in general explosive.

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Table I. Elemental Analysis of a Series of hfac Complexes of Co(III)

complex	formula (M_r)	found (calcd), %		
		C	H	N
[Co(en) ₂ (hfac)](ClO ₄) ₂	CoC ₉ H ₁₇ O ₁₆ N ₄ Cl ₂ F ₆ (585.1)	18.30 (18.48)	2.85 (2.93)	9.55 (9.58)
[Co(NH ₃) ₄ (hfac)](ClO ₄) ₂	CoC ₅ H ₁₃ O ₁₀ N ₄ Cl ₂ F ₆ (533.0)	11.08 (11.27)	2.71 (2.46)	10.36 (10.51)
α -[Co(trien)(hfac)](ClO ₄) ₂	CoC ₁₁ H ₁₉ O ₁₀ N ₄ Cl ₂ F ₆ (611.1)	21.45 (21.62)	3.33 (3.13)	9.04 (9.17)
β -[Co(trien)(hfac)](ClO ₄) ₂ ·H ₂ O	CoC ₁₁ H ₂₁ O ₁₁ N ₄ Cl ₂ F ₆ (629.1)	21.09 (21.00)	3.30 (3.36)	9.02 (9.05)
<i>fac</i> (N)-[Co(i-dtma)(hfac)]ClO ₄	CoC ₁₁ H ₁₅ O ₈ N ₃ ClF ₆ (525.6)	25.03 (25.14)	3.13 (2.88)	8.09 (7.99)
<i>mer</i> (N)-[Co(i-dtma)(hfac)]ClO ₄	CoC ₁₁ H ₁₅ O ₈ N ₃ ClF ₆ (525.6)	25.33 (25.14)	2.92 (2.88)	8.03 (7.99)
α -[Co(edda)(hfac)]	CoC ₁₁ H ₁₁ O ₆ N ₂ F ₆ (440.2)	29.97 (30.01)	2.46 (2.52)	6.41 (6.37)
β -[Co(edda)(hfac)]	CoC ₁₁ H ₁₁ O ₆ N ₂ F ₆ (440.2)	29.92 (30.01)	2.47 (2.52)	6.52 (6.37)

Table II. UV-Visible Absorption Maxima of a Series of hfac Complexes of Co(III) in Water and in Basic Medium

complex	pH of medium	color	λ_{\max} , nm	ϵ_{\max} , M ⁻¹ cm ⁻¹	λ_{\max} , nm	ϵ_{\max} , M ⁻¹ cm ⁻¹	λ_{\max} , nm	ϵ_{\max} , M ⁻¹ cm ⁻¹
[Co(en) ₂ (hfac)](ClO ₄) ₂	<5	orange	487	139	350	2500		
	>10	pink	523	130				
[Co(NH ₃) ₄ (hfac)](ClO ₄) ₂	<5	red-orange	494	84.0	347	2920		
	>10	pink	534	90.6				
α -[Co(trien)(hfac)](ClO ₄) ₂	<5	orange	486	142.4	350	2580		
	>10	red-violet	524	128.0				
β -[Co(trien)(hfac)](ClO ₄) ₂ ·H ₂ O ^a	<5	orange	488	225	350	2140		
	>10	red-violet	521	191				
<i>fac</i> (N)-[Co(i-dtma)(hfac)]ClO ₄	<5	pink	513	182.0	349	2600		
	>10	violet	553	139.6				
<i>mer</i> (N)-[Co(i-dtma)(hfac)]ClO ₄	<5	orange	493	150.6	353	2480		
	>10	red-violet	537	129.0				
α -[Co(edda)(hfac)]	<5	red-violet	550	154	346	2400	232	25 000
	>10	blue	575	155	~345 (sh)	~900	234	23 000
β -[Co(edda)(hfac)]	<5	pink	507	226	352	2200	230	25 000
	>10	blue-violet	558	224	~385 (sh)	~230	232	23 000

^a Contaminated with a small fraction of the α isomer—see NMR data.

¹H, ¹³C, and ¹⁹F NMR spectra were recorded on Varian XL 100, Bruker WH 270, and Nicolet NT 300 WB spectrometers at the University of Frankfurt. Further experimental details are given in the appropriate sections.

Results and Discussion

The purity of the synthesized hfac complexes is underlined by the analytical data in Table I. In addition, the NMR spectra (see further discussion) also clearly proved this to be the case. The *mer*(N) and *fac*(N) isomers of the i-dtma complex were assigned on the basis of the preparative procedure employed. The *mer*(N) isomer was obtained by reacting *fac*(N)-[Co(i-dtma)(H₂O)₂](ClO₄)₂ with hfac in the presence of active carbon at 100 °C. These drastic conditions are necessary for the rearrangement of the coordinated i-dtma ligand. In contrast, the *fac*(N) isomer was prepared by the reaction of the corresponding diaquo species with hfac at 40 °C in the absence of activated carbon. Furthermore, the UV-visible absorption spectra of these species are in close agreement with those of the corresponding acetylacetonato (acac) complexes, which have been characterized by ¹H NMR spectroscopy.⁸ The α and β isomers of the edda complex were assigned on the basis of their UV-visible spectral data (Table II). In all cases the assignments were underlined by the NMR spectra.

The UV-visible spectra of the hfac complexes show some interesting features. First of all, the absorption maximum of the first band of a hfac complex always lies at a lower wavelength than for the corresponding acac complex,⁸ demonstrating the stronger ligand field of the hfac complex. Second, the band around 350 nm can be assigned to the $t_{2g}(\text{metal}) \rightarrow \pi^*(\text{ligand})$ transition, in agreement with a similar transition at 325 nm for the corresponding acac complexes. The lowering of the π^* energy level in the case of the hfac ligand may be attributed to the strong electronegativity of the fluorine atoms. Third, large spectral changes occur in basic medium: the first band shifts to considerably higher wavelength (by ca. 40 nm), and the characteristic band around 350 nm vanishes in most cases. These spectral changes are completely reversible under moderate conditions. Some secondary decomposition reactions (loss of hfac ligand) were observed over longer periods of time in strongly basic media (pH ≥ 12).

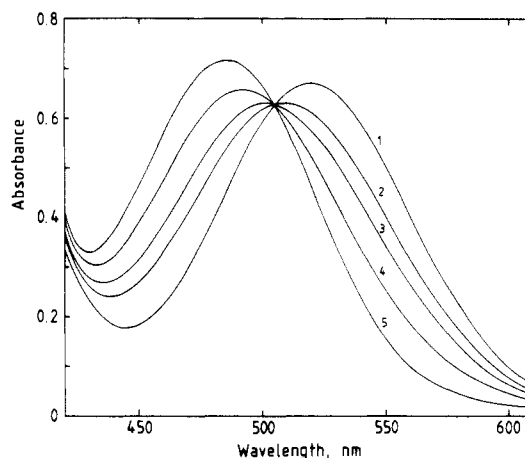


Figure 1. Visible absorption spectra for the equilibrium $\text{Co(en)}_2(\text{hfac})^{2+} + \text{OH}^- \rightleftharpoons \text{Co(en)}_2(\text{hfacOH})^+$ (temp = 25 °C; ionic strength 1.0 M; optical path length 1 cm; [Co(III)] = 0.01 M): (1) pH 10.92; (2) pH 8.35; (3) pH 8.02; (4) pH 7.51; (5) pH 1.69.

Table III. pH Titration of α -[Co(trien)(hfac)](ClO₄)₂^a

v (OH ⁻), ^b mL	pH	$10^{-6} \times$ K_1 , ^c M ⁻¹	v (OH ⁻), ^b mL	pH	$10^{-6} K_1$, ^c M ⁻¹
0	5.11		0.6	7.50	4.72
0.1	6.37	4.63	0.7	7.71	4.51
0.2	6.72	4.72	0.8	7.96	4.36
0.3	6.96	4.66	0.9	8.32	4.28
0.4	7.15	4.70	1.0	9.50	
0.5	7.32	4.76			
mean 4.6 ± 0.2					

^a Conditions: temp = 25 °C; ionic strength ~12 mM; $K_W = 1.01 \times 10^{-14}$. ^b Quantity of 0.1 M KOH added to 25 mL of a 0.004 M complex solution. ^c Estimated from $K_1 = v/(1-v)[\text{OH}^-]$.

The very distinct pH dependence of the UV-visible absorption spectra is ascribed to the addition of hydroxide to the hfac ligand

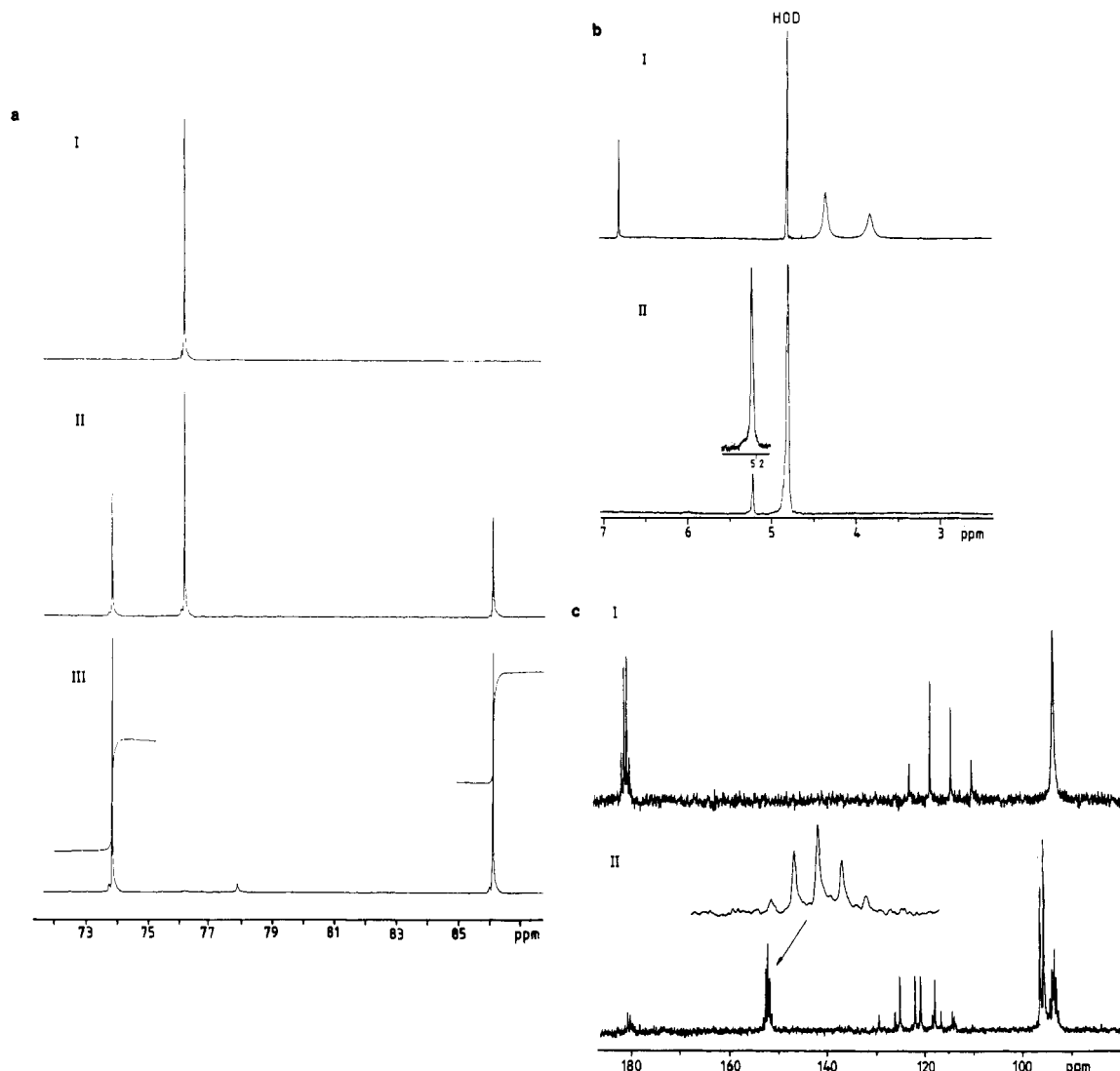


Figure 2. (a) ^{19}F NMR spectra of $\text{Co}(\text{NH}_3)_4(\text{hfac})^{2+}$ at 94 MHz in D_2O : (I) pH 6; (II) pH 8; (III) pH 9. (b) ^1H NMR spectra of $\text{Co}(\text{NH}_3)_4(\text{hfac})^{2+}$ at 300 MHz in D_2O : (I) pH 6; (II) pH 8.5. (c) ^1H -broad-band-decoupled ^{13}C NMR spectra of $\text{Co}(\text{NH}_3)_4(\text{hfac})^{2+}$ at 67.9 MHz in $\text{Me}_2\text{SO}-d_6$ and D_2O : (I) pH 6; (II) pH 8.

as shown in reaction 1. Equilibrium constants for this reaction were determined in two ways: by standard pH titration of a 0.004 M complex solution with a 0.1 M base solution and from a spectrophotometric analysis of the complex solution in the presence of Tris buffer (Tris = tris(hydroxymethyl)aminomethane) as a function of pH. Typical examples of both methods are given in Table III and Figure 1, respectively, and the results are summarized in Table IV. K_1 shows a significant temperature dependence for the *fac*(N) isomer of the *i*-dtma complex, from which it follows¹¹ that $\Delta H^\circ = -33 \pm 2 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = 7 \pm 7 \text{ J K}^{-1} \text{ mol}^{-1}$. The magnitude of K_1 is such that the $\text{p}K_a$ values ($K_a = K_1 K_w$) of the hfac complexes vary between 7.3 and 9.0 at 25 °C. These values are significantly higher than the $\text{p}K_a$ values normally reported for aquo complexes of Co(III),¹² indicating that the hydrolysis step does not involve the formation of ring-opened aquo complexes. The large difference in the K_1 values for α -Co-(trien)(hfac)²⁺ can only be ascribed to ionic strength and/or buffer effects.

We now turn to a discussion of the NMR data. The most symmetrical complex within the series investigated is the $\text{Co}(\text{NH}_3)_4(\text{hfac})^{2+}$ species. The ^{19}F NMR spectrum at 94 MHz in D_2O exhibits only one intense signal at 76.15 ppm, indicating that

both CF_3 groups experience identical fields. Addition of NaOD to pH ~ 8 , i.e. close to the $\text{p}K_1$ value reported in Table IV, results in a decrease in this signal and the appearance of two new signals shifted to 2.33 ppm lower and 9.88 ppm higher fields, respectively (see Figure 2a). At higher pH, where eq 1 is completely shifted to the right, only the new singlets at 73.82 and 86.03 ppm are observed. The high-field signal is ascribed to the CF_3 group attached to the carbon atom undergoing OH^- addition. Furthermore, the new singlets are exactly in the ratio 1:1 as would be expected for such an addition process. The ^1H NMR spectrum (Figure 2b) exhibits trends similar to those reported before⁴ for the $\text{Co}(\text{en})_2(\text{hfac})^{2+}$ species. The singlet at 6.81 ppm disappears on the addition of base, and a new singlet shows up at 5.23 ppm. The ammine signals at 3.8 and 4.4 ppm disappear due to H/D exchange. The ^1H -broad-band-high-power decoupled ^{13}C spectrum of $\text{Co}(\text{NH}_3)_4(\text{hfac})^{2+}$ in $\text{D}_2\text{O}-\text{Me}_2\text{SO}-d_6$ (7:3) at pH ~ 6 (Figure 2c) exhibits a CH singlet at 91.46 ppm, a CO quartet at 176 ppm ($^2J_{\text{CF}} = 38 \text{ Hz}$), and one CF_3 quartet at 115 ppm ($^1J_{\text{CF}} = 280 \text{ Hz}$). At pH ~ 8.5 the spectrum exhibits additional resonances: a CH singlet at 94 ppm, two CO quartets at 150 and 92 ppm (due to CO and OCOH, respectively¹³), and two CF_3 quartets at 122

(11) In this calculation the temperature parameters of K_w are taken as $\Delta H^\circ = 55.8 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = -80.7 \text{ J K}^{-1} \text{ mol}^{-1}$ from: Ootaki, H.; Tanaka, M.; Funahashi, S. "Yoeki-hanno No Kagaku"; Gakkai Shuppan Center: Tokyo, 1977; p 46.

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Table IV. Values of K_1 for a Series of hfac Complexes of Co(III)^a

complex	$10^{-6}K_1, {}^b M^{-1}$	
	method A	method B
Co(NH ₃) ₄ (hfac) ²⁺	5.0 ± 0.4 (23)	3.4 ± 0.2 (25, λ = 550 nm)
Co(en) ₂ (hfac) ²⁺	3.0 ± 0.2 (23)	1.10 ± 0.02 (25, λ = 540 nm)
α-Co(trien)(hfac) ²⁺	4.6 ± 0.2 (25)	0.49 ± 0.06 (25, λ = 470 nm)
β-Co(trien)(hfac) ²⁺	2.3 ± 0.3 (25)	1.09 ± 0.01 (25, λ = 470 nm)
fac(N)-Co(i-dtma)(hfac) ⁺	5.0 ± 0.2 (19)	
	3.0 ± 0.1 (15)	
	1.3 ± 0.0 (30)	
	0.7 ± 0.1 (45)	
mer(N)-Co(i-dtma)(hfac) ⁺	2.5 ± 0.2 (25)	
α-Co(edda)(hfac)	0.09 ± 0.01 (25)	
β-Co(edda)(hfac)	0.83 ± 0.07 (25)	

^a $K_1 = [\text{CoL}(\text{hfacOH})]/[\text{CoL}(\text{hfac})][\text{OH}^-]$. Determined in two ways: method A, pH titration as in Table III, ionic strength ≤ 12 mM; method B, spectrophotometric method as in Figure 1, ionic strength 1.0 M, [Tris] = 0.5 M. ^b Data measured at temperatures quoted in parentheses (°C).

Table V. NMR Data (ppm) for a Series of hfac Complexes of Co(III) and Their Conjugated Bases

complex	¹⁹ F	¹ H (C-H)	¹³ C [J, Hz]
Co(NH ₃) ₄ (hfac) ²⁺	76.15	6.81	CO: 177.74, 177.21, 176.68, 176.16 [² J _{CO,F} = 36] CF ₃ : 121.28, 117.1, 112.90, 108.72 [¹ J _{CF} = 284] CH: 91.46
at pH ~8.5	73.82, 86.03	5.23	CO(I): 150.5, 150.09, 149.66, 149.22 [² J _{CO,F} = 29.7] CO(II): 92.84, 92.42, 91.98, 91.70 [² J _{CO,F} = 29.9] CF ₃ (I,II): 124.98, 123.59, 120.86, 119.30 [¹ J _{CF} = 280]; 117.28, 116.74, 113.10, 112.62 [¹ J _{CF} = 300] CH: 93.84
Co(en) ₂ (hfac) ²⁺	76.32	6.80	CO: 181.96, 180.42, 180.87, 180.33 [² J _{CO,F} = 37] CF ₃ : 123.20, 119.02, 114.85, 110.69 [¹ J _{CF} = 283] CH: 94.8
at pH ~9	73.82, 73.91, 85.90, 86.13	5.21, 5.17	C-C: 45.8, 48.5 CO(I): 153.18, 152.72, 152.27, 152.03, 151.82, 151.36 [² J _{CO,F} = 30.6] CO(II): 94.56, 94.11, 93.95, 93.66, 93.25, 92.80 [² J _{CO,F} = 30.7] CF ₃ (I,II): 129.4, 126.1, 125.2, 122.2, 120.9, 118.0, 116.8, 113.9 CH: 97.5, 96.5
complex	¹⁹ F	¹ H (C-H)	
α-Co(trien)(hfac) ²⁺	76.33	6.79	
at pH ~9.5	74.03, 85.88, 86.25	5.28, 5.22	
β-Co(trien)(hfac) ²⁺	76.34, 76.44	6.82	
at pH ~9	73.82, 73.96, 74.2, 85.65, 85.83, 85.98, 86.42	5.95, 5.26, 5.21, 5.12	
fac(N)-Co(i-dtma)(hfac) ⁺	75.93, 76.36	6.79, 6.72	
at pH ~9	73.13, 73.23, 74.08, 74.17, 84.46, 85.04, 85.64, 86.11	5.13, 5.82, 5.43, 5.91	
mer(N)-Co(i-dtma)(hfac) ⁺	75.81, 75.87	6.72	
at pH ~9	73.22, 73.74, 85.08, 86.05	5.31, 5.72	

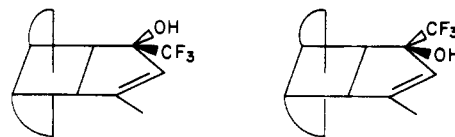
ppm (¹J_{CF} = 280 Hz) and 119 ppm (¹J_{CF} = 300 Hz). These spectra could not be recorded at higher pH values where all of the starting material would have been converted to the hydrolyzed form, since slow subsequent decomposition (loss of hfac) occurs under such conditions during the long data accumulation time required for such spectra.

The spectra in Figure 2 exhibit similar tendencies and demonstrate that no diastereomers are produced during the addition of OH⁻ to the hfac ligand of such a symmetrical complex. During the addition of OH⁻ to one of the two carbonyl carbon atoms in coordinated hfac, the chelate ring presumably does not deviate significantly from its original planar structure while the carbon atom changes to a tetrahedral geometry. In this configuration the OH and CF₃ groups point into the same direction away from the metal center, but to opposite sides of the chelate plane (a similar notation has been adopted in the structural drawings given in the remainder of this paper). It follows that the C-OH bond can occupy a position above or below the plane of the hfac ligand. These two positions facilitate the production of different stereochemical isomers during the addition process, depending on the symmetry of the overall complex. In the case of the tetraammine species these are optical isomers and do not show up in the NMR spectra.

Finally, it should be mentioned that the completely different shifts observed for the CF₃ (¹⁹F spectra) and CO (¹³C spectra) groups upon addition of base to the complex underline the earlier

suggestion of OH addition to the CO carbon atom of the coordinated ligand. A similar process has also been observed for the uncoordinated (free) ligand.¹⁴

Evidence for the formation of different diastereomers in basic solution was found in the case of the Co(en)₂(hfac)²⁺ species. The ¹⁹F NMR spectrum exhibits a sharp singlet at 76.32 ppm in acidic medium, corresponding to two equivalent CF₃ groups. This resonance disappears on the addition of base, and two singlets (intensity ratio 44:56) appear at 2.40 and 2.33 ppm lower field and another two (intensity ratio 56:44) at 9.58 and 9.80 ppm higher field. Further addition of NaOD causes the signal of the starting complex to disappear completely (see Figure 3a), whereas addition of DCl reverses the process. These spectra indicate that two diastereomers (ratio 44:56) are produced when OH⁻ (or OD⁻) binds to one of the carbonyl carbon atoms, and these can be presented as



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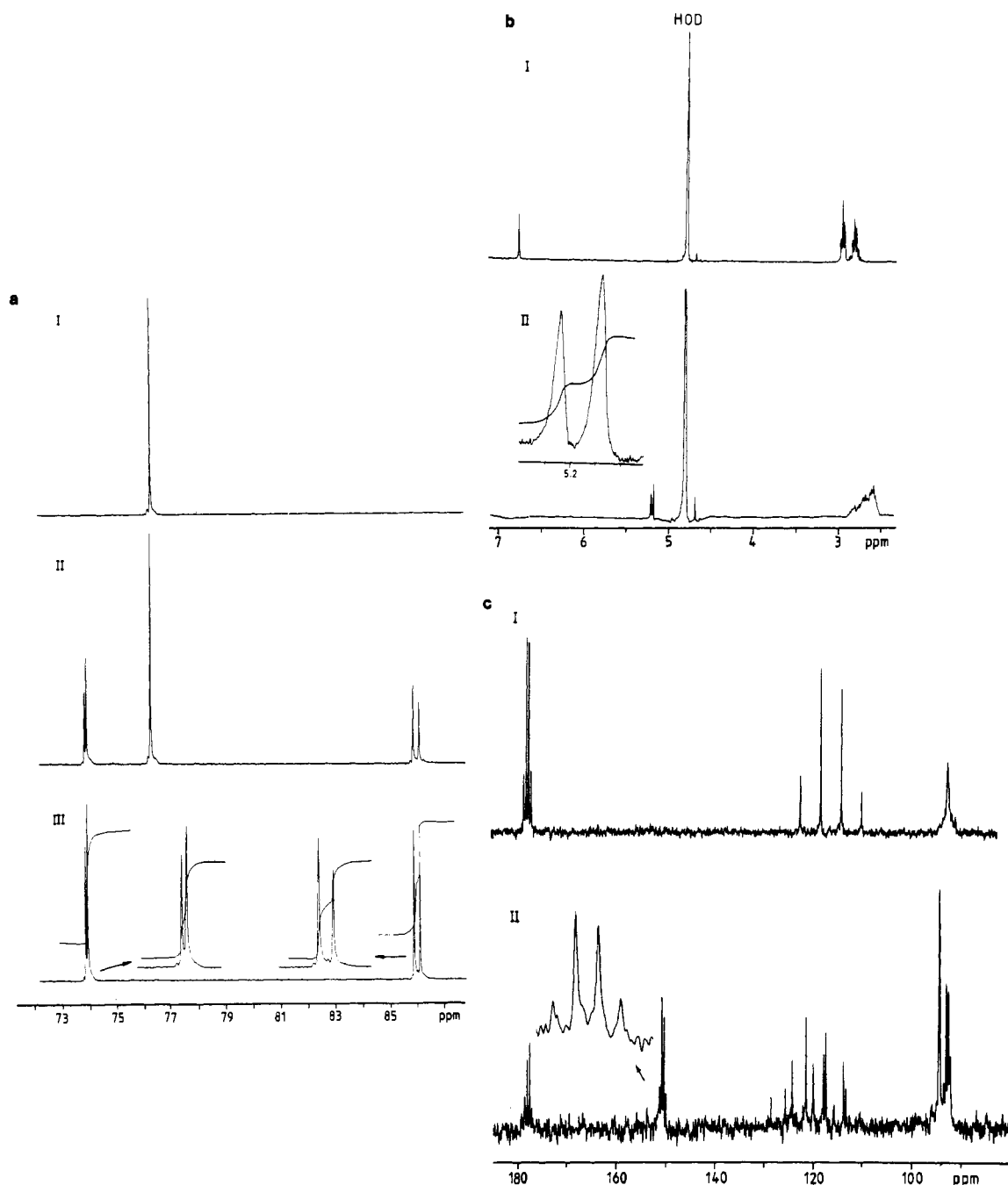


Figure 3. (a) ^{19}F NMR spectra of $\text{Co}(\text{en})_2(\text{hfac})^{2+}$ at 94 MHz in D_2O : (I) pH 6; (II) pH 7.5; (III) pH 9. (b) ^1H NMR spectra of $\text{Co}(\text{en})_2(\text{hfac})^{2+}$ at 300 MHz in D_2O : (I) pH 6; (II) pH 9. (c) ^1H -broad-band-decoupled ^{13}C NMR spectra of $\text{Co}(\text{en})_2(\text{hfac})^{2+}$ at 67.9 MHz in D_2O : (I) pH 6; (II) pH 9.

Addition of OH^- to the other carbonyl atom results in isomeric species equivalent to those given above. The occurrence of two diastereomers is further confirmed by the ^1H spectra in Figure 3b. The starting complex exhibits a single peak at 6.7 ppm for the methine proton and different peaks between 3 and 2.7 ppm for the ethylenediamine ligand. Addition of base (pH \sim 9) produces two signals for the methine proton at 5.2 and 5.17 ppm, respectively, and these exhibit the intensity ratio of 44:56 as found for the ^{19}F spectra. Very similarly the ^1H -broad-band-decoupled ^{13}C spectrum in D_2O at pH \sim 6 exhibits a quartet of two equivalent CO groups ($^2J_{\text{CO,F}} = 37$ Hz), a quartet of two equivalent CF_3 groups ($^1J_{\text{CF}} = 283$ Hz), and a singlet for the methine carbon atom (see Figure 3c). When these coupling constants are compared with those of trifluoroacetic acid¹³ ($^2J_{\text{CO,F}} = 44$ Hz, $^1J_{\text{CF}} = 283$ Hz), trifluoropropanol ($^2J_{\text{CO,F}} = 32$ Hz, $^1J_{\text{CF}} = 283$ Hz), and related compounds, it is seen that $^2J_{\text{CO,F}}$ for $\text{Co}(\text{en})_2(\text{hfac})^{2+}$ lies between the characteristic values for a $\text{C}=\text{O}$ and a $\text{C}-\text{OH}$ group, indicating that the CO group has a mixed

bond character in this complex. After addition of base the spectrum (Figure 3c) exhibits two different CO groups as quartets at 153 and 94.5 ppm. Both these quartets appear as double signals, and the observed shifts depend on the experimental conditions employed during these measurements. The methine carbon also shows two singlets at 96.5 and 97.5 ppm, respectively. The ethylene carbon atoms appear as two sharp symmetric singlets at 45.8 and 48.5 ppm (not shown in Figure 3c). Addition of base results in an unsymmetric multiplet similar to that reported before.⁴ It follows that all the NMR observations underline the formation of two diastereomers on the addition of OH^- to $\text{Co}(\text{en})_2(\text{hfac})^{2+}$.

The ^{19}F NMR spectrum of α -[$\text{Co}(\text{trien})(\text{hfac})](\text{ClO}_4)_2$ dissolved in D_2O exhibits characteristics very similar to those for the corresponding ethylenediamine complex (see Table V). The α -trien complex also belongs to the C_2 point group, and two possible isomers can be produced during the addition of hydroxide to the carbonyl carbon atom. The two low-field singlets coincide at 74.03 ppm but are of exactly the same intensity as those at 85.88

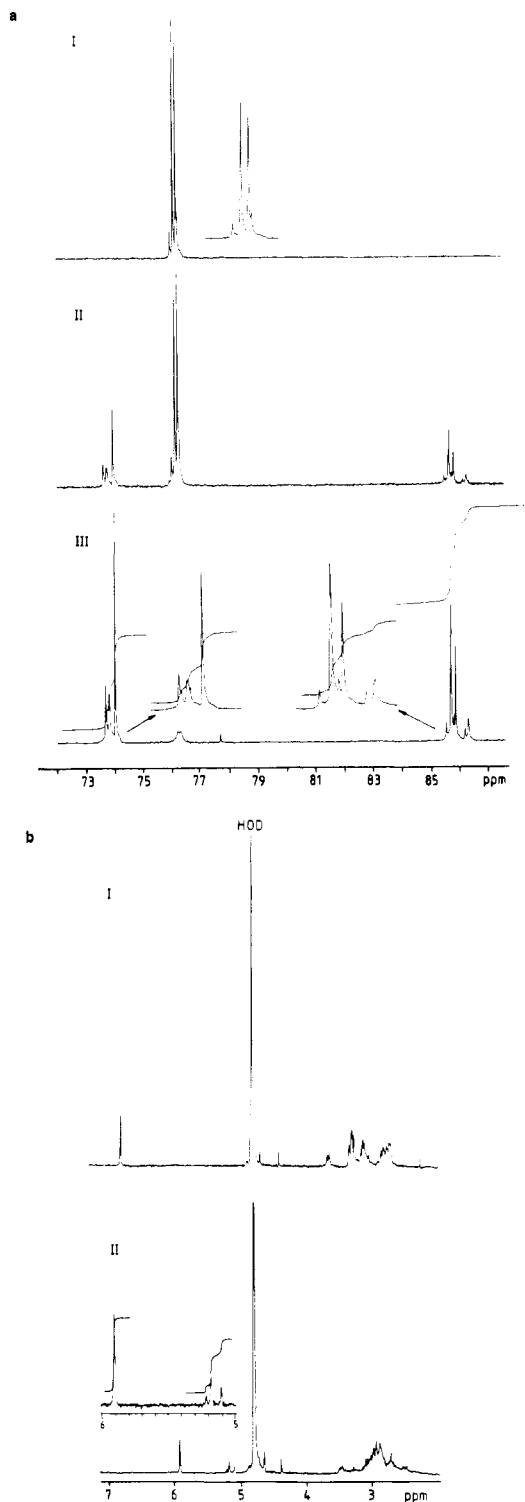
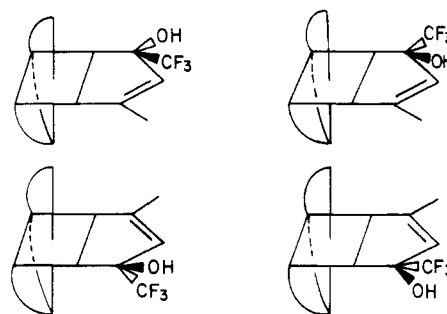


Figure 4. (a) ^{19}F NMR spectra of $\beta\text{-Co}(\text{trien})(\text{hfac})_2^{2+}$ at 94 MHz in D_2O : (I) pH 6.5; (II) pH 8; (III) pH 9. (b) ^1H NMR spectra of $\beta\text{-Co}(\text{trien})(\text{hfac})_2^{2+}$ at 270 MHz in D_2O : (I) pH 6.5; (II) pH 9.5.

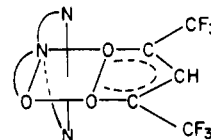
and 86.25 ppm. The latter signals reveal an isomeric ratio of 66:34. A similar tendency was seen in the ^1H spectrum of the methine proton, which shifts from 6.79 to 5.28 and 5.22 ppm, with an intensity ratio of 34:66, when base is added to the trien complex. In contrast the ^{19}F spectrum of $\beta\text{-[Co}(\text{trien})(\text{hfac})](\text{ClO}_4)_2$ in D_2O and pH ~ 6.5 (see Figure 4a) exhibits two sharp signals of almost equivalent intensity at 76.34 and 76.44 ppm, respectively. The small resonances at 76.22 and 76.48 ppm are ascribed to weak proton-fluorine coupling. Similar effects show up in almost all the other ^{19}F spectra reported in this study. The $\beta\text{-trien}$ complex belongs to the C_1 point group, and although only one isomeric form is possible, the two CF_3 groups experience different fields.¹⁵

Addition of OH^- can result in the formation of two isomers for each carbonyl center, thus a total of four diastereomers:



The ^{19}F spectrum exhibits three low-field singlets at 73.82, 73.95, and 74.2 ppm and four upfield singlets at 85.33, 85.65, 85.98, and 86.42 ppm, respectively. These resonances can be ascribed to the mentioned isomeric forms, where the low-field signal at 74.2 ppm is the overlap of two singlets similar to that observed for the α isomer. The more intense peak at 76.34 ppm and additional peaks at 85.91 and 86.30 ppm are due to a minor impurity of the α isomer present in the sample (see Table V). A similar tendency is observed in the ^1H spectrum (Figure 4b), where the signal for the methine proton at 6.82 ppm is shifted to produce four singlets at 5.95, 5.26, 5.21, and 5.12 ppm during the addition of base. These signals once again confirm the presence of four diastereomers when OH^- adds on to the hfac ligand coordinated to the $\beta\text{-trien}$ complex. The ratio of the four isomers is 57:6:24:12.

In the case of the $\text{mer}(N)\text{-Co}(\text{i-dtma})(\text{hfac})^+$ complex the two CF_3 groups are not equivalent and show up as two almost similar singlets in the ^{19}F spectrum at 75.87 and 75.81 ppm. It follows from the following diagram that this complex has a plane of symmetry (the COONOC plane):



Attachment of OH^- to one of the carbonyl atoms above or below this plane does not give rise to geometrical isomers. The ^{19}F signals shift on the addition of base to 73.22 and 73.74 ppm at low field and 85.08 and 86.05 ppm at high field with ratios of 40:60 and 60:40, respectively. The ^1H spectrum also confirms the formation of two diastereomers on the addition of base with resonances at 5.15 and 5.80 ppm. The $\text{fac}(N)\text{-Co}(\text{i-dtma})(\text{hfac})^+$ complex belongs to the C_1 point group, and the two CF_3 groups are not equivalent. This clearly shows up in the ^{19}F spectrum, where resonances occur at 75.93 and 76.36 ppm. Addition of base produces four diastereomers (see Table V), similar to those for the $\beta\text{-trien}$ complex. The intensity ratio of the ^{19}F signals is 70:18:6:6. A very similar effect is observed in the ^1H spectrum, and four resonances (intensity ratio 19:69: ~ 5 : ~ 5) occur on the addition of base.

The overall comparison of the NMR data in Table V clearly underlines the similarity in behavior of the different complexes investigated. These data are also in good agreement with data recently reported for a hfac complex of $\text{Pd}(\text{II})$.¹⁶ Furthermore, the results of this investigation not only underline earlier suggestions⁴ concerning the addition of base to the coordinated hfac ligand but also reveal interesting information regarding the various coordination geometries of such addition products. The employed NMR techniques are indeed powerful tools for the elucidation

- (15) A reviewer kindly drew our attention to the fact that two isomeric forms of this complex are possible, viz. the so-called $\text{cis-}\beta_1$ and $\text{cis-}\beta_2$ isomers, where the meridional secondary NH proton can either be adjacent to, or remote from, the coordinated hfac oxygen. However, we do not expect this relatively small difference to show up in the recorded spectra and prefer to ascribe the small resonances to weak proton-fluorine coupling as for the other investigated complexes.
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of complex isomeric mixtures and for the characterization of such reaction products.

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Registry No. hfac, 1522-22-1; [Co(en)₂(hfac)](ClO₄)₂, 69496-10-2; Co(en)₂(hfac)²⁺, 69496-09-9; [Co(NH₃)₄(hfac)](ClO₄)₂, 94090-17-2; Co(NH₃)₄(hfac)²⁺, 94090-16-1; α-[Co(trien)(hfac)](ClO₄)₂, 94090-19-4; α-Co(trien)(hfac)²⁺, 94090-23-0; β-[Co(trien)(hfac)](ClO₄)₂, 94233-40-6; β-Co(trien)(hfac)²⁺, 94160-59-5; *fac*(N)-[Co(i-dtma)(hfac)]ClO₄, 94090-21-8; *fac*(N)-Co(i-dtma)(hfac)⁺, 94090-20-7; *mer*(N)-[Co(i-dtma)(hfac)]ClO₄, 94233-41-7; *mer*(N)-Co(i-dtma)(hfac)⁺, 94160-60-8; α-[Co(edda)(hfac)]₂, 94090-22-9; β-[Co(edda)(hfac)]₂, 94198-89-7; *fac*(N)-[Co(i-dtma)(H₂O)₂](ClO₄)₂, 94160-58-4; α-[Co(edda)(H₂O)₂]ClO₄, 32715-40-5.

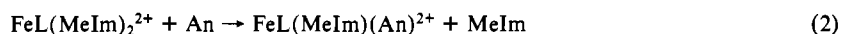
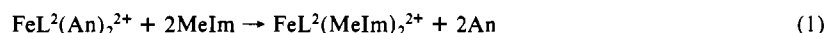
Contribution from the Department of Chemistry,
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Axial Labilization by Macrocyclic Ligands. 4. Further Studies of Axial Substitution in Low-Spin Iron(II) Complexes Containing 14-Membered Tetraaza Macrocyclic Ligands

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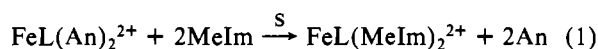
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The results of studies of the kinetics of reactions 1 and 2 in acetone solvent are presented. Here, L is any of five tetraaza-tetraimine

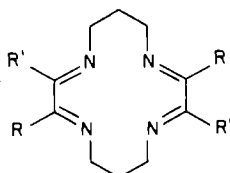
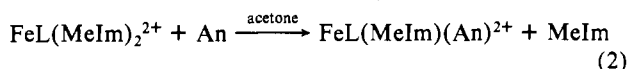


macrocyclic ligands and L² = a specific one of these ligands, An = acetonitrile, and MeIm = *N*-methylimidazole. The limiting first-order rate constant for reaction 1, determined under pseudoorder conditions with use of the usual integrated first-order rate expression, is 24 s⁻¹ at 30 °C. Limiting first-order rate constants for reaction 2, determined by the method of initial rates, range from 6.1 × 10⁻³ to 2.1 × 10⁻¹ s⁻¹ at 30 °C, depending upon the identity of the macrocyclic ligand, L. The results indicate that the substitutions occur via the dissociative (D) mechanism. The dissociative rate and activation parameters (obtained from the temperature dependence of the limiting first-order rate constants) vary with the structure of the macrocyclic ligand in a manner consistent with our previous findings.

Axial ligand substitution reactions of metal ions in macrocyclic ligand environments have engendered much study, since they are obviously relevant to bioinorganic systems incorporating a metal-porphyrin moiety.¹⁻¹² We have been particularly interested in the relationship between the structure of a macrocyclic ring system and its ability to labilize the axial sites of the metal ion. We have attempted to examine this relationship in three previous papers, in which we have reported the results of studies of the kinetics of substitution of axial acetonitrile by *N*-methylimidazole in a variety of low-spin, synthetic macrocyclic ligand complexes of iron(II).¹⁰⁻¹² The reactions investigated are indicated in general form in reaction 1 (L = any of six macrocyclic ligands,¹⁰⁻¹² An = acetonitrile, and S = solvent = acetone). Herein, we report



the results of one additional study of this type, involving the macrocyclic ligand L².¹³ In addition, we report the results of kinetics studies of reaction 2, for all systems indicated. As for



L	R	R'
L ¹	CH ₃	CH ₃
L ²	CH ₃	Ph
L ³	<i>p</i> -MeOPh	<i>p</i> -MeOPh
L ⁴	<i>p</i> -MePh	<i>p</i> -MePh
L ⁵	Ph	Ph

the previously investigated systems, reactions 1 and 2 proceed by the dissociative (D) mechanism. Dissociative rate constants and the associated activation parameters, Δ*H*[‡] and Δ*S*[‡], are correlated with the donor ability of the macrocyclic ligand, as represented quantitatively by *E*_{1/2}(Fe^{II}-Fe^{III}), the half-wave redox potential for the reduction of Fe(III) to Fe(II) in the appropriate series of complexes.

Experimental Section

Reagents. Reagent grade acetonitrile, acetone, and *N*-methylimidazole were dried and/or purified as previously described.^{10,11} All other materials were reagent grade and were used without further purification.

Syntheses. FeL¹(An)₂(PF₆)₂¹⁴ and FeL²(An)₂(PF₆)₂¹⁵ were synthesized according to literature methods. FeL(An)₂(PF₆)₂, L = L³-L⁵, were synthesized as described previously.^{10,11}

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