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Spectroscopic and Structural Studies of the Unique Hydrolysis Product of a Hexafluoroacetylacetonato Complex of Cobalt(III). Crystal Structure of Bis(ethylenediamine)(hexafluorohydroxyethylacetonato)cobalt(III) Bromide Hydrate, $[Co(en)_2(hfacOH)]Br \cdot H_2O$

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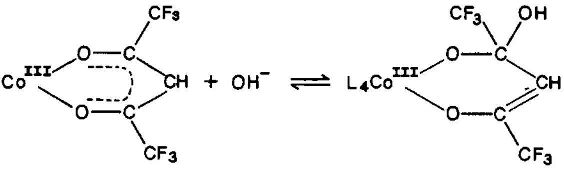
Earlier kinetic and spectroscopic studies of the hydrolysis reaction of the title complex suggested the reversible addition of hydroxide to the carbonyl carbon atom of the hexafluoroacetylacetonato ligand. The hydrolysis product has now been isolated, and a crystal structure of the bromide salt is reported: $C_9H_{18}BrCoF_6N_4O_3 \cdot H_2O$, a = 8.65 (1) Å, b = 10.13 (1) Å, c = 21.02 (2) Å, β = 97.21 (7)°, monoclinic, $P2_1/c$, Z = 4. This underlines the validity of the earlier conclusions. A surprising feature of this structure is that the Co–N bonds are significantly longer (1.969 (3) and 1.977 (3) Å) when they are opposite to an oxygen atom than in the other case (1.953 (3) and 1.944 (3) Å). Furthermore, the length of the single C–C bond of one of the ethylenediamine ligands is far too short (1.366 (8) Å) and indicates significant disorder in the structure. In addition, detailed spectroscopic (^1H, ^{13}C, and ^{19}F NMR) measurements on the isolated and closely related complexes were performed, and the results are discussed in reference to the earlier findings.

Introduction

We recently reported a detailed study[4] on the synthesis and identification of a series of hexafluoroacetylacetonato (hfac) complexes of Co(III) and the spectroscopic analyses of the reversible addition of hydroxide to the coordinated ligand in aqueous solution. The overall process can be summarized as in (1), where



(1)

L_4 = $(NH_3)_4$, $(en)_2$, α- and β-edda, α- and β-trien, and *mer*(*N*)- and *fac*(*N*)-i-dtma (en = ethylenediamine, edda = ethylenediaminediacetate, trien = triethylenetetramine, and i-dtma = 4-diethylenetriaminemonoacetate). Evidence for the addition of OH^- to the coordinated ligand came from ^1H, ^{13}C, and ^{19}F NMR data,[4,5] which also indicated the existence of different isomers in solution in the case of the nonsymmetrical L_4 groups. In addition we performed a detailed kinetic study of reaction 1 using stopped-flow and temperature-jump techniques at normal[6] and at elevated pressures.[7] The spectroscopic and kinetic results all underlined the validity of the formulation given in (1). However, we were never able to isolate this unique hydrolysis product to unequivocally prove its structure.

In a subsequent study[8] we set out to directly observe the C–OH bond in the hydrolysis product by using ^{17}O NMR techniques and used $[Co(en)_2(hfac)]Br_2$ as the starting material instead of the perchlorate salt. Addition of base, quite surprisingly, resulted in the precipitation of the hydrolysis product. Suitable crystals for an X-ray structure analysis[2] were obtained by recrystallization. In addition, detailed spectroscopic measurements on the isolated complex and related ones (other L_4 groups), also isolated as the bromo salts, were performed. The results reported in this paper unequivocally prove the general validity of reaction 1.

Experimental Section

The complex $[Co(en)_2(hfac)]Br_2$ was prepared by adding NaBr to a concentrated aqueous solution of $[Co(en)_2(hfac)](ClO_4)_2$.[9] Addition of an equimolar concentration of NaOH to a concentrated solution of this complex caused the characteristic color change associated with reaction 1. Addition of a concentrated solution of NaBr resulted in the crystallization of the hydrolysis product, and the obtained crystals were dried over P_2O_5. Chemical analyses were in excellent agreement with the composition $[Co(en)_2(hfacOH)]Br \cdot H_2O$. Other complexes isolated in a similar way are $[Co(NH_3)_4(hfacOH)]Br$ and β-$[Co(trien)(hfacOH)]Br$.

^1H, ^{13}C, and ^{19}F NMR spectra were recorded on Varian XL 100 and Bruker AM 300 spectrometers. The crystal structure of $[Co(en)_2(hfacOH)]Br \cdot H_2O$ was determined by X-ray diffraction. The sample was recrystallized from methanol, and a dark red needle of dimensions 0.1 × 0.05 × 0.5 mm³ was sealed in a Lindemann glass capillary. A total of 24 reflections with $2\theta > 20°$ (Mo Kα radiation) were used for cell refinement: a = 8.65 (1) Å, b = 10.13 (1) Å, c = 21.02 (2) Å, β = 97.21 (7)°, monoclinic, $P2_1/c$, M_r = 501.11, V = 1827.3 Å³, Z = 4, D_{exptl} = 1.821 Mg m^{-3}, T = 293 K, μ = 26.4 cm^{-1}. The esd's of the cell constants are larger than expected because the crystals decompose in the X-ray beam. One hemisphere of data was collected (h, −11 to 11; k, 0 to 13; l, −27 to 27; agreement between the two asymmetric units 1.4%) with $\theta_{\min}$ = 2° and $\theta_{\max}$ = 28°: Nicolet R3 computer-controlled diffractometer, λ = 0.7107 Å, graphite monochromator, two standard reflections ((130) and (404)) showing an intensity decay of 5.9% (for this relatively small amount of decay no correction was made), ω scan at rates varying between 4.5 and 20° min^{-1}, 3942 of the 4438 unique reflections with $I > \sigma(I)$, data reduction including corrections for Lorentz, polarization, background (profile fitting), and absorption effects. The last were based on χ scans of a few reflections (range of transmission factors 0.21–0.26); there was no extinction correction. The phase problem was solved by a Patterson synthesis and successive difference Fourier syntheses of electron density. In the final refinement the positions of the hydrogen atoms were refined by using a model with idealized geometry (C–H = 0.96 Å, N–H = 0.90 Å) and temperature factors fixed at 1.2 times the equivalent isotropic values for the C and N atoms to which they were attached. The H atom at the oxygens could be found experimentally. In the least-squares refinement on F (minimizing $\sum w(F_o - F_c)^2$) with 3942 data and 229 parameters all the other atoms could be refined anisotropically; $w = 1/\sigma^2(F)$, R = 0.087, and R_2 (=R_w) = 0.032 (w according to the counting statistics). The 10 largest peaks in a final difference electron density synthesis were between 0.53 and 0.77 e Å^{-3}. All calculations were performed with a Nova 3/12 computer using SHELXTL;[10] the scattering factors and f' were taken from ref 11. The X-ray powder diffraction pattern was measured with a counter Guinier diffractometer (Huber, Rimsting (Chiemsee), West Germany; Cu Kα_1 radiation, α-quartz

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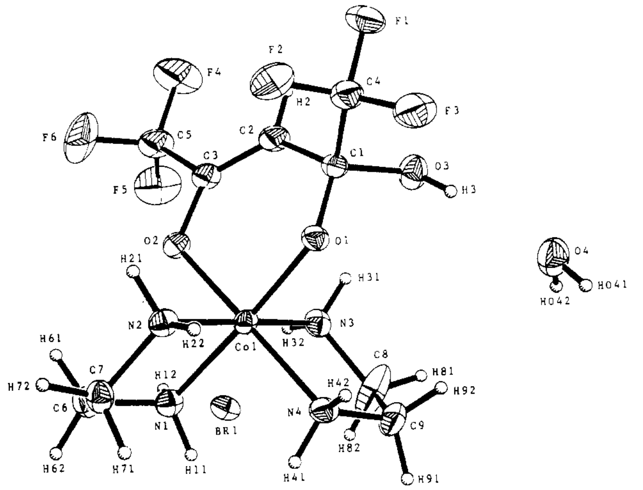

Figure 1. Molecular structure of [Co(en)$_2$(hfacOH)]Br·H$_2$O, showing 20% probability thermal ellipsoids for the non-hydrogen atoms and the atom-numbering scheme.

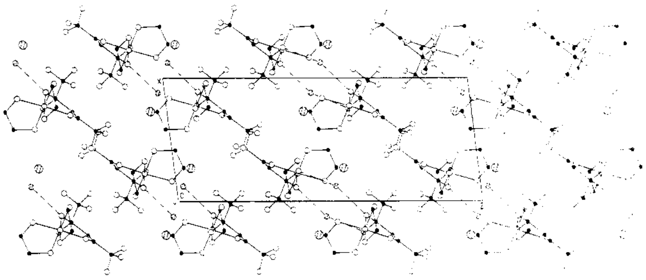

Figure 2. Projection of the crystal structure along *b*.

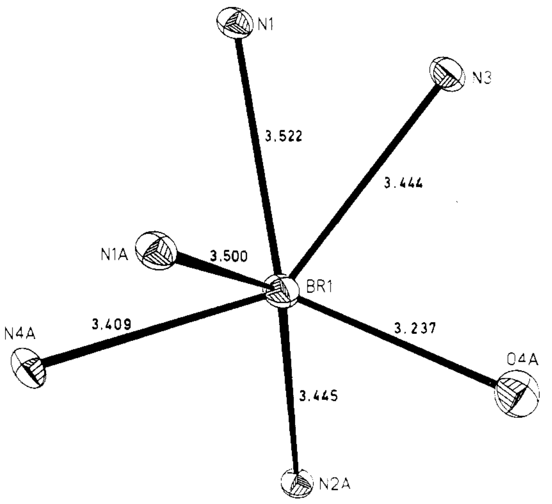

Figure 3. Coordination sphere of the bromide ion. The atomic distances are given in Å.

monochromator); the calculated pattern was obtained by the SHELXTL program system.

Results and Discussion

Crystal Structure Determination. Details of the molecular and crystal structure of [Co(en)$_2$(hfacOH)]Br·H$_2$O are summarized in Figures 1–3 and Tables I and II. It can be seen that the hydroxy group is bonded to C1. Co(III) has an octahedral coordination geometry. The Co–N bonds are significantly longer (1.969 (3) and 1.977 (3) Å) when they are trans to an oxygen atom than in the other case (1.953 (3) and 1.944 (3) Å). The two oxygen atoms are distorting the regular octahedron. The atoms of the plane O1, O2, N1, N4 are much more out of plane (0.072 Å) than the atoms of the planes O1, N1, N2, N3 and O2, N2, N3, N4 (0.008 and 0.004 Å, respectively).

Table I. Atomic Coordinates and Coefficients of the Isotropic Temperature Factors[a]

atom	*x*	*y*	*z*	*B*
Br1	0.72990 (5)	0.09684 (5)	0.44532 (2)	4.45 (2)
Co1	0.22690 (6)	0.21368 (5)	0.40070 (2)	2.98 (2)
F1	0.0549 (4)	0.6615 (3)	0.2974 (1)	7.5 (1)
F2	−0.0657 (3)	0.4768 (3)	0.2880 (1)	7.3 (1)
F3	−0.0697 (3)	0.5921 (3)	0.3727 (1)	7.7 (1)
F4	0.4470 (4)	0.4360 (3)	0.2128 (2)	10.7 (2)
F5	0.5658 (4)	0.2840 (4)	0.2654 (2)	9.6 (1)
F6	0.3760 (4)	0.2387 (4)	0.1997 (1)	10.8 (2)
O1	0.1127 (3)	0.3735 (2)	0.3903 (1)	3.5 (1)
O2	0.2975 (3)	0.2233 (3)	0.3199 (1)	3.9 (1)
O3	0.2452 (4)	0.5723 (3)	0.4056 (2)	5.5 (1)
O4	0.1227 (4)	0.6137 (3)	0.5220 (2)	6.2 (1)
N1	0.3279 (4)	0.0382 (3)	0.4062 (1)	3.8 (1)
N2	0.0437 (4)	0.1195 (3)	0.3599 (2)	3.5 (1)
N3	0.4122 (4)	0.3027 (3)	0.4418 (2)	4.1 (1)
N4	0.1650 (4)	0.2013 (3)	0.4875 (1)	3.9 (1)
C1	0.1650 (5)	0.4803 (4)	0.3607 (2)	3.7 (1)
C2	0.2721 (5)	0.4562 (4)	0.3110 (2)	4.5 (1)
C3	0.3217 (5)	0.3382 (4)	0.2953 (2)	3.9 (1)
C4	0.0228 (7)	0.5533 (5)	0.3299 (2)	5.4 (2)
C5	0.4278 (6)	0.3251 (5)	0.2433 (2)	6.0 (2)
C6	0.2352 (5)	−0.0521 (4)	0.3617 (2)	4.3 (1)
C7	0.0666 (5)	−0.0239 (4)	0.3669 (2)	4.1 (1)
C8	0.4160 (6)	0.2896 (8)	0.5120 (2)	9.3 (3)
C9	0.2732 (7)	0.2731 (5)	0.5321 (2)	7.2 (2)

[a] The atomic coordinates are given in units of the lattice constants; the isotropic temperature coefficients (in Å^2) were calculated from the anisotropic ones after the last least-squares cycle. The esd's are in parentheses. $B = 8\pi^2(\text{trace } \tilde{U})/3$.

Table II. Bond Lengths (in Å) and Bonding Angles (in deg)[a]

Co1–O1	1.895 (3)	O2–C3	1.301 (5)
Co1–O2	1.877 (3)	O3–C1	1.441 (5)
Co1–N1	1.977 (3)	N1–C6	1.471 (5)
Co1–N2	1.953 (3)	N2–C7	1.470 (5)
Co1–N3	1.944 (3)	N3–C8	1.478 (6)
Co1–N4	1.969 (3)	N4–C9	1.436 (6)
F1–C4	1.339 (6)	C1–C2	1.501 (6)
F2–C4	1.339 (6)	C1–C4	1.510 (7)
F3–C4	1.337 (6)	C2–C3	1.326 (6)
F4–C5	1.314 (6)	C3–C5	1.519 (7)
F5–C5	1.294 (6)	C6–C7	1.504 (6)
F6–C5	1.305 (6)	C8–C9	1.366 (8)
O1–C1	1.354 (5)		
Co1–O1–C1	122.5 (3)	O1–C1–C2	117.4 (3)
Co1–O2–C3	119.5 (3)	O1–C1–C4	106.7 (4)
Co1–N1–C6	108.7 (2)	O2–Co1–N1	84.7 (1)
Co1–N2–C7	110.3 (2)	O2–Co1–N2	88.1 (1)
Co1–N3–C8	108.4 (3)	O2–Co1–N3	92.0 (1)
Co1–N4–C9	110.1 (3)	O2–Co1–N4	176.8 (1)
F1–C4–F2	106.0 (4)	O2–C3–C2	129.4 (4)
F1–C4–F3	106.4 (4)	O2–C3–C5	110.5 (4)
F1–C4–C1	114.2 (4)	O3–C1–C2	105.8 (3)
F2–C4–F3	105.8 (4)	O3–C1–C4	105.3 (3)
F2–C4–C1	111.5 (4)	N1–Co1–N2	85.1 (1)
F3–C4–C1	112.3 (4)	N1–Co1–N3	93.3 (1)
F4–C5–F5	106.5 (4)	N1–Co1–N4	93.3 (1)
F4–C5–F6	106.4 (4)	N1–C6–C7	107.0 (3)
F4–C5–C3	113.7 (4)	N2–Co1–N3	178.4 (1)
F5–C5–F6	104.9 (4)	N2–Co1–N4	94.3 (1)
F5–C5–C3	112.5 (4)	N2–C7–C6	107.5 (3)
F6–C5–C3	112.2 (4)	N3–Co1–N4	85.6 (1)
O1–Co1–O2	94.3 (1)	N3–C8–C9	114.4 (4)
O1–Co1–N1	174.1 (1)	N4–C9–C8	113.6 (4)
O1–Co1–N2	89.1 (1)	C1–C2–C3	124.5 (4)
O1–Co1–N3	92.5 (1)	C2–C1–C4	108.7 (3)
O1–Co1–N4	87.9 (1)	C2–C3–C5	120.1 (4)
O1–C1–O3	112.2 (3)		

[a] Esd's are given in parentheses.

The cobalt atom is lying 0.633 Å above the plane C1, C2, C3, O1, O2. The Co1–O2 and O2–C3 distances (1.877 and 1.301 Å, respectively), are much smaller than the corresponding Co1–O1

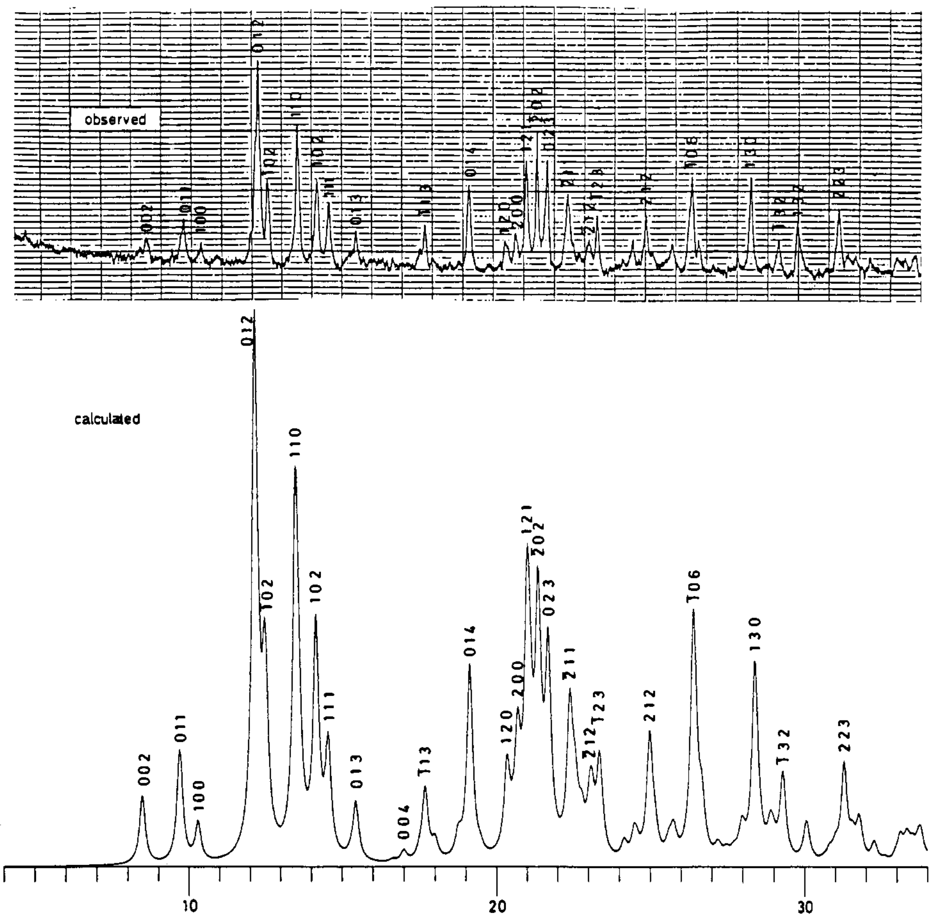

Figure 4. Calculated and measured powder X-ray diffraction patterns.

and O1–C1 distances (1.895 and 1.354 Å, respectively). This is surely a mesomeric effect of the C2–C3 double bond, notwithstanding the fact that this bond is not enlarged.

The length of the single bond C8–C9 is far too short (1.366 Å). As can be seen from the figures and the tables, C8 and to a smaller degree C9 have unusually large temperature coefficients. This means there is disorder in this part of the molecule, and the unusual bond distances exhibit artifacts. A possible reason for this may be the very weak intramolecular hydrogen bonds N3–H31···O3 (3.138 Å) and O3–H3···O4 (2.817 Å).

The crystal structure is shown in Figure 2. It is seen that the compound produces dimers by two bridging water molecules. The hydrogen bonds are O1···O4 (2.916 Å) and O3···O4 (2.817 Å). The bromide ions have very distorted octahedral surroundings, which are shown along with the distances in Figure 3. The positively charged molecular ions are connected by hydrogen bonds from the water molecules and are parallel to (102). The bromide ions are between these sheets.

The calculated and the measured powder X-ray diffraction patterns are compared in Figure 4. It can be seen that only one crystal phase was present in the crystallized sample.

Spectroscopic Measurements. The powder diffraction results reported in the previous part clearly indicate that the isolated $[Co(en)_2(hfacOH)]Br{\cdot}H_2O$ complex exists in only one isomeric form in the solid state. In our earlier study,[4] however, the $[Co(en)_2(hfacOH)]^+$ species was prepared in solution and the ^1H, ^{13}C, and ^{19}F NMR spectra indicated the presence of two stereochemical isomers: the OH and CF_3 groups point into the same direction away from the metal center but to opposite sides of the chelate plane such that the C–OH bond can occupy a position above or below the plane of the hfac ligand. These isomers will be mirror images in the case of a symmetrical amine ligand such as for the corresponding tetraammine complex. However, in the present case the ethylenediamine ligands introduce an asymmetric environment and different isomers are produced by the configurations of the CF_3 and OH groups coordinated to the hfac ligand. Since the ^1H NMR spectrum was recorded in D_2O by performing the hydrolysis reaction in this medium, only the methine proton could be observed, which exhibited two signals at 5.20 and 5.17 ppm (ratio 44:56). With the isolated bromide salt, ^1H NMR spectra for the OH group could be recorded in DMF-d_7, Me_2SO-d_6, and acetone-d_6. The results in Table III clearly demonstrate that the signals originating from the OH group also indicate the presence of two isomers in the case of the ethylenediamine complex.

Table III. ^1H and ^{19}F NMR Data for $[Co(en)_2(hfacOH)]Br$ and $[Co(NH_3)_4(hfacOH)]Br$ in Various Solvents

complex	solvent	^{19}F NMR, ppm	^1H NMR, ppm	isomeric ratio
$[Co(en)_2$-$(hfacOH)]Br$	acetone-d_6	71.26, 71.21 83.63, 83.97	4.07, 4.67 (OH) 4.89, 4.92 (OH)	33:67
	Me_2SO-d_6	69.60, 69.66 81.72, 82.39	4.84, 5.52 (OH) 4.77 (CH)	25:75
	DMF-d_7	71.55, 71.53 83.67, 84.18	4.75, 5.58 (OH) 4.84, 4.87 (CH)	43:57
	D_2O	73.87, 73.94 85.90, 86.14	5.21, 5.17 (CH)	43:57
$[Co(NH_3)_4$-$(hfacOH)]Br$	acetone-d_6	71.27 83.65	4.44 (OH) 4.92 (CH)	

The ratio of these isomers depends on the nature of the solvent, the concentration of the complex, and the temperature of the solution. Measurements indicated that the isomeric equilibrium ratio is usually reached within a few minutes after dissolution. In general only small temperature effects were observed (Table IV), from which it can be concluded that the reaction enthalpy for this equilibration is small and non-zero. In Me_2SO-d_6 as solvent the isomeric ratio of 25:75 reaches an equilibrium value of 41:59 at 25 °C. It follows from the results in Tables III and IV that the nature of the medium has a significant influence on the ratio of the isomers. By way of comparison, the ^1H NMR spectrum of $[Co(NH_3)_4(hfacOH)]Br$ (see Table III) does not indicate the presence of any isomers, which is in agreement with

Table IV. Temperature Dependence of the Isomeric Ratio of [Co(en)$_2$(hfacOH)]$^+$ in Various Solvents

solvent	temp, °C	isomeric ratio[a]
acetone-d_6	40	32:68
	30	33:67
	22	33:67
	0	35:65
	-10	35:65
	-20	35:65
	-30	34:66
	-40	34:66
	-50	34:66
	-60	34:66
CH_3OD[b]	10	28:72
	0	28:72
	-10	29:71
	-20	28:72
	-30	25:75
	-40	24:76
	-50	23:77
	-60	22:78
DMF-d_7	60	41:59
	40	41:59
	20	43:57
	10	44:56
	0	44:56
	-15	45:55

[a] Mean value of at least two determinations. [b] In this case the hydrolysis product is [Co(en)$_2$(hfacOCH$_3$)]$^+$, which could be isolated (see ref 8).

the expected situation since the position of the OH group will not lead to different isomers as in the case of the ethylenediamine complex.

Some typical ^{1}H NMR spectra are reported in Figure 5. The spectrum of [Co(en)$_2$(hfac)]$^{2+}$ in acetone-d_6 exhibits a sharp signal for the methine proton at 6.4 ppm and four different broad signals for the amine groups at 6.78, 6.65, 6.22, and 5.38 ppm. The latter signals are broadened due to ^{14}N–^{1}H interactions over one or more bonds, i.e. $^1J_{NH}$ and $^2J_{NCH}$. The ^{1}H NMR spectrum of [Co(en)$_2$(hfacOH)]Br in acetone-d_6 indicates two sharp signals for the methine proton at 4.89 and 4.92 ppm, two sharp signals for the OH proton at 4.08 and 4.64 ppm (ratio 67:33), and a number of broad signals originating from the unsymmetrical NH$_2$ groups (Figure 5a). The same spectrum recorded 1 h later (Figure 5b) indicates the decrease in the signals for the OH group due to slow H/D exhange with the solvent in basic medium. Addition of one drop of D$_2$O results in the immediate disappearance of these signals followed by a slow H/D exchange of the amine protons (Figure 5c).

With the pure sample of [Co(en)$_2$(hfacOH)]Br·H$_2$O now available, a high resolution ^{1}H broad band high power decoupled ^{13}C spectrum could be recorded (Figure 6). A similar but not so well resolved spectrum was reported before,[4] but unfortunately the spectra in Figures 2c and 3c of that paper[4] were interchanged during printing. Spectra recorded in a D$_2$O–Me$_2$SO-d_6 mixture exhibit two different CO signals, both as a quartet of double signals that appear as a pentet at 152.15 ($^2J_{CO(I),F}$ = 30.6 Hz) and 93.60 ppm ($^2J_{CO(II),F}$ = 30.4 Hz, OH-attached CO group). The double signals originate from the presence of two isomers in solution and can be observed as separated signals when pure Me$_2$SO-d_6 is used as solvent.

The methine carbon atom also shows two signals at 95.5 and 96.5 ppm, whereas the two CF$_3$ groups appear as two different quartets of double signals between 114 and 128 ppm, respectively ($^1J_{CF(I)}$ = 289.2 Hz and $^1J_{CF(II)}$ = 278.5 Hz). The unsymmetrical ethylene carbons show up as six sharp signals of varying intensity between 44 and 47 ppm.

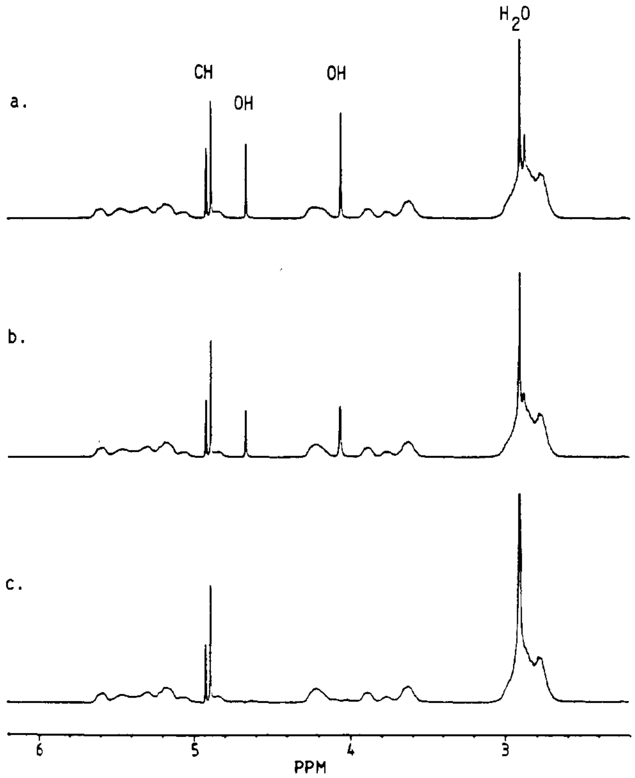

Figure 5. ^{1}H NMR spectra of [Co(en)$_2$(hfacOH)]Br in acetone-d_6: (a) 5 min after dissolution; (b) 60 min after dissolution; (c) H/D exchange following addition of D$_2$O.

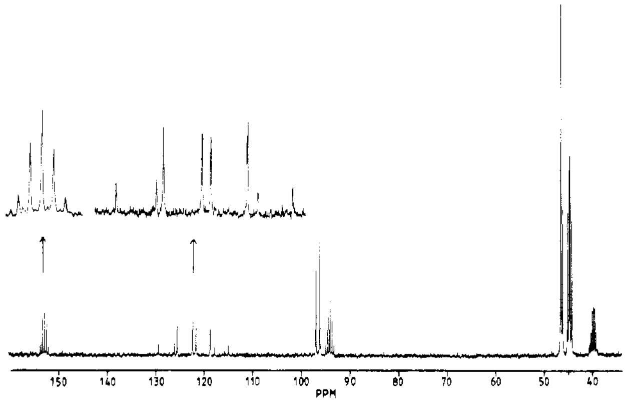

Figure 6. ^{1}H broad band decoupled ^{13}C NMR spectrum of [Co(en)$_2$(hfacOH)]Br in D$_2$O–Me$_2$SO-d_6.

The NMR results clearly indicate that, depending on the nature of the L$_4$ ligand, different isomeric forms of the hydrolysis product are present in solution. Furthermore, these isomers appear to exist in a fairly rapid equilibration, which is temperature- and solvent-dependent, since dissolution of a nonisomeric solid sample (see Crystal Structure Determination) immediately exhibits evidence for the presence of isomers. In addition, we must conclude that the one isomeric form in the case of the ethylenediamine complex must be significantly less soluble than the other to account for the fact that only one isomer is present in the solid sample isolated. Our kinetic study[6] has demonstrated that the addition and reverse elimination of OH$^-$ are rapid processes (on a milli- or microsecond time scale depending on the pH of the solution), from which we conclude that the coordinated hydroxy ligand is very labile and so can account for the rapid equilibration of the isomeric mixture during isolation or dissolution of the hydrolysis product.

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Supplementary Material Available: Tables of temperature coefficients, bond lengths and angles with hydrogen atoms, and torsion angles (9 pages); a list of structure factors (24 pages). Ordering information is given on any current masthead page.