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Spectrophotometric Study of the Methoxide Addition to Hexafluoroacetylacetonato Complexes of Co(III) and the Crystal Structure of β-[Co(trien)-(hfacOCH$_3$)](ClO$_4$)

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Abstract

In methanolic solution, a rapid and reversible methoxide addition occurs to a hexafluoroacetylacetonato (hfac) ligand on a Co(III) complex. The equilibrium constant of this reaction was estimated by visible spectrophotometry.

β-[Co(trien)(hfacOCH$_3$)]ClO$_4$ was synthesized by means of the reaction between β-Co(trien)(hfac)$^{2+}$ and OCH$_3^-$ in the presence of ClO$_4^-$ ions (trien = triethylenetetramine). It crystallized in the triclinic space group $P\bar{1}$ with $a = 9.073(2)$, $b = 10.138(1)$, $c = 12.011(1)$ Å, $\alpha = 94.19(1)$, $\beta = 111.90(2)$, $\gamma = 94.63(1)°$ and $Z = 2$. The structure was determined from 2710 observed reflections. The final R value was 0.080.

Introduction

In a recent report, it has been suggested from NMR evidence that a complex Co(en)$_2$(hfacOCH$_3$)$^+$ is formed when [Co(en)$_2$(hfacOH)]Br·H$_2$O is dissolved in CH$_3$OD [1]. This methoxide addition to a coordinated hfac ligand on a Co(III) complex is unprecedented. In the present work, we intend to clarify this phenomenon in more detail by UV–Vis spectroscopy and X-ray crystallography.

Experimental

Materials

Commercially available reagents, triethylamine hydrochloride (TEAHCl) (Kanto, G.R.), triethylamine (TEA) (Wako, ≳99%), sodium methylate (Wako, 28% in methanol) and hydrogen chloride–methanol (Tokyo Kasei) were used. The concentrations of HCl or NaOCH$_3$ in methanol were determined by titration, where potassium biphthalate was used as primary standard and phenolphthalein as indicator. The water content of the methanolic solution was determined by the Karl–Fischer titration. It was below 0.05 wt% for solvent methanol, for TEA + TEAHCl buffer, and for 0.01 M NaOCH$_3$; 0.11 wt% for 0.005 M HCl (M = mol dm^{-3}). The complex compounds were obtained and identified as in a previous work [2]. β-[Co(trien)(hfac)]-(ClO$_4$)$_2$ was dissolved in methanol. Slight excess of methanolic solution of NaOCH$_3$ and a small amount of NaClO$_4$ were added successively to this solution. After some while, β-[Co(trien)(hfacOCH$_3$)]-ClO$_4$ crystallized in this solution.

Structure Analysis

The reddish-violet compound (β-[Co(trien)(hfacOCH$_3$)]ClO$_4$, C$_{12}$H$_{22}$N$_4$O$_7$ClCoF$_6$) molecular weight = 543.7 g mol^{-1} crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.073(2)$, $b = 10.138(1)$, $c = 12.011(1)$ Å, $\alpha = 94.19(1)$, $\beta = 111.90(2)$, $\gamma = 94.63(1)°$, $Z = 2$, $D_{\text{exp}} = 1.79$ and $D_{\text{calc}} = 1.778$ g cm^{-3}. The three dimensional intensity data were collected for θ values between 3° and 26° on a Enraf-Nonius CAD4F diffractometer using graphite monochromated Mo Kα radiation. A crystal with dimensions 0.10 × 0.16 × 0.15 mm was used for the data collection. No decomposition of the crystal was detected during the data collection. A total of 3963 reflections were measured of which 2710 were considered as observed ($I > 3\sigma(I)$). The data were collected for Lorentz, polarization and absorption effects.

The structure was solved by means of Patterson and Fourier methods. The final R value converged to 0.080 using all the observed reflections and anisotropic thermal parameters for all the non-hydrogen atoms. The final positional parameters with their estimated standard deviations are listed in Table I. The interatomic bond distances and bond angles are given in Table II. See also 'Supplementary Material'.

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TABLE I. Positional (×10^4) and Thermal Parameters (×10^3) for β-[Co(trien)(hfacOCH$_3$)]ClO$_4$

Atom	x	y	z	U_{eq}^{a}
Co	1453(1)	2601(1)	2535(1)	40.0(6)
N(1)	2755(8)	4312(7)	2721(6)	48(4)
C(11)	3813(10)	4197(9)	2022(8)	53(5)
C(12)	2910(11)	3189(9)	920(8)	56(5)
N(2)	2350(8)	1972(7)	1361(6)	49(4)
C(13)	3687(11)	1138(9)	1946(9)	58(5)
C(14)	3477(12)	623(9)	3056(9)	60(6)
N(3)	3140(8)	1817(7)	3715(6)	49(4)
C(15)	2626(13)	1504(10)	4719(9)	66(6)
C(16)	1936(12)	2770(10)	5015(8)	62(6)
N(4)	758(9)	3122(7)	3845(6)	51(4)
O(1)	177(7)	950(5)	2231(6)	50(3)
O(2)	−106(6)	3417(5)	1376(5)	46(3)
C(1)	−2138(13)	−358(10)	2011(10)	62(6)
C(2)	−1378(10)	884(8)	1746(8)	47(5)
C(3)	−2323(11)	1736(9)	1091(8)	53(5)
C(4)	−1650(11)	2953(9)	722(9)	51(5)
O(41)	−2675(8)	3989(7)	583(7)	69(4)
C(41)	−2398(15)	4801(12)	1677(11)	85(9)
C(5)	−1829(12)	2616(10)	−635(10)	60(6)
F(11)	−1626(9)	−1435(5)	1691(7)	99(5)
F(12)	−3684(8)	−542(8)	1519(10)	136(7)
F(13)	−1756(13)	−399(7)	3167(7)	133(7)
F(51)	−1005(7)	1610(6)	−713(5)	70(4)
F(52)	−1212(8)	3636(6)	−1022(6)	81(4)
F(53)	−3329(7)	2291(6)	−1378(6)	76(4)
Cl(1)	2578(3)	6942(2)	4856(2)	53(1)
O(11)	3875(9)	6162(8)	5096(8)	85(5)
O(12)	2839(18)	7910(13)	4221(14)	194(13)
O(13)	1129(10)	6208(9)	4163(10)	112(7)
O(14)	2577(13)	7538(13)	5929(10)	145(10)

$^aU_{eq} = \frac{1}{3}\Sigma_i\Sigma_j[U_{ij}(a_i^*a_j^*)(\vec{a}_i\vec{a}_j)]$

TABLE II. Selected Interatomic Distances (Å) and Bond Angles (°) for β-[Co(trien)(hfacOCH$_3$)]ClO$_4$^{a}

Bond	Distance (Å)	Bond	Distance (Å)
Co–N(1)	1.967(7)	C(1)–C(2)	1.50(1)
Co–N(2)	1.966(9)	C(2)–C(3)	1.35(1)
Co–N(3)	1.930(7)	C(2)–O(1)	1.30(1)
Co–N(4)	1.956(8)	C(3)–C(4)	1.50(1)
Co–O(1)	1.886(5)	C(4)–C(5)	1.59(2)
Co–O(2)	1.874(5)	C(4)–O(2)	1.35(1)
N(1)–C(11)	1.50(1)	C(4)–O(41)	1.44(1)
C(11)–C(12)	1.53(1)	O(41)–C(41)	1.42(1)
C(12)–N(2)	1.50(1)	C(1)–F(11)	1.31(1)
N(2)–C(13)	1.52(1)	C(1)–F(12)	1.29(1)
C(13)–C(14)	1.54(2)	C(1)–F(13)	1.30(1)
C(14)–N(3)	1.51(1)	C(5)–F(51)	1.33(1)
N(3)–C(15)	1.49(1)	C(5)–F(52)	1.33(1)
C(15)–C(16)	1.55(2)	C(5–F(53)	1.32(1)
C(16)–N(4)	1.50(1)		

(continued)

TABLE II. *(continued)*

Angle	(°)	Angle	(°)
N(1)–Co–N(2)	86.6(3)	O(1)–C(2)–C(3)	130.3(8)
N(2)–Co–N(3)	86.3(3)	C(2)–C(3)–C(4)	121.9(8)
N(3)–Co–N(4)	86.8(3)	C(3)–C(4)–O(2)	117.1(7)
N(4)–Co–N(1)	94.3(3)	C(4)–O(2)–Co	128.8(5)
O(1)–Co–O(2)	94.8(2)	C(2)–O(1)–Co	120.4(5)
N(1)–Co–O(1)	175.7(3)	O(2)–C(4)–O(41)	111.7(7)
N(3)–Co–O(2)	177.1(3)	C(5)–C(4)–O(41)	100.2(7)
N(2)–Co–N(4)	173.1(3)	C(5)–C(4)–O(2)	107.6(9)
C(1)–C(2)–O(1)	110.7(7)	C(4)–O(41)–C(41)	114.0(8)

^{a}e.s.d.s given in parentheses.

Results and Discussion

Color Change

When an orange colored complex [Co(en)$_2$(hfac)]-(ClO$_4$)$_2$ is dissolved in methanol, an orange colored solution is formed. If one adds a methanolic solution of NaOCH$_3$ to this solution, its color immediately changes to pink. By a successive addition of a methanolic solution of HCl, the color returns to the original one. A similar color change can also be observed for several Co(III) complexes containing an hfac ligand. This reversible color change is quite analogous to that observed in aqueous solutions of these complexes on addition of NaOH and HCl [2]. We consider that this color change in methanolic solution is caused by a shift of the equilibrium

$$\mathrm{CoL_4(hfac)^{n+} + OCH_3^- \rightleftharpoons CoL_4(hfacOCH_3)^{n-1}} \quad (1)$$

where L$_4$ represents ligands occupying the remaining four coordination sites.

Spectrophotometry

In Fig. 1, the visible absorption spectra of a methanolic solution of [Co(en)$_2$(hfac)](ClO$_4$)$_2$ are shown. Spectrum (1) in basic medium differs significantly from Spectrum (3). The latter is the same as that with HCl additive. In TEA + TEAHCl buffer, an intermediate spectrum (2) is obtained and one can estimate the equilibrium constant. For analogous complexes, the absorption peaks in methanolic solution are summarized in Table III. The visible spectra of the complex were recorded in 0.005 M HCl or 0.01 M NaOCH$_3$, where the concentrations of the complex [Co(III)] were 0.0006 ~ 0.0051 M and the optical path length was 1 cm. These solutions were diluted by methanol and the UV spectra were recorded. For each complex, in basic medium the first band shifts to considerably higher (35 ~ 60 nm) wavelength and the characteristic band around 350 nm vanishes.

TABLE III. Absorption Peaks of Methanolic Solution of $[CoL_4(hfac)](ClO_4)_x$

L_4 [a]	Medium	λ_{max} (nm) (ϵ)				Color
$(en)_2$	$[HCl]/[Co(III)] = 1.0$	485 (151)	350 (2510)	285 (3450)sh		orange
	$[NaOCH_3]/[Co(III)] = 2.0$	520 (142)	380 (175)sh		225 (15300)sh	pink
$(NH_3)_4$	$[HCl] = 0.005$ M [b]	493 (87)	345 (2670)	285 (2910)	230 (15800)sh	orange
	$[NaOCH_3]/[Co(III)] = 1.9$	530 (92)	380 (153)sh		226 (12600)sh	pink
α-(trien)	$[HCl]/[Co(III)] = 1.0$	484 (154)	347 (2420)			orange
	$[NaOCH_3]/[Co(III)] = 2.0$	517 (139)	380 (173)sh		230 (15700)sh	pink
β-(trien)	$[HCl]/[Co(III)] = 1.5$	486 (238)	348 (2170)		235 (22200)	orange
	$[NaOCH_3]/[Co(III)] = 3.4$	524 (195)	380 (212)sh		226 (17900)sh	pink
f(N)-(i-dtma)	$[HCl]/[Co(III)] = 1.1$	513 (212)	350 (2530)		235 (27000)	pink
	$[NaOCH_3]/[Co(III)] = 2.7$	560 (159)	380 (330)sh		218 (19600)	violet
α-(edda)	$[HCl]/[Co(III)] = 6.3$	550 (158)	360 (1950)sh		235 (25000)	violet
	$[NaOCH_3]/[Co(III)] = 9.3$	595 (133)	400 (222)sh		235 (21000)	blue
β-(edda)	$[HCl]/[Co(III)] = 8.0$	510 (218)	350 (1990)		235 (22500)	violet
	$[NaOCH_3]/[Co(III)] = 13.2$	566 (172)	395 (196)sh	300 (9166)	235 (16400)sh	blue

[a] i-dtma = 4-diethylenetriaminemonoacetate, edda = ethylenediaminediacetate. [b] Solution was diluted by 0.005 M HCl.

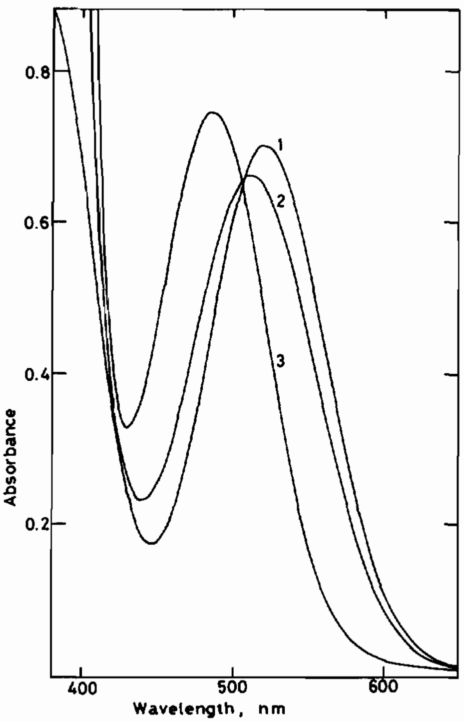

Fig. 1. Visible absorption spectra for the equilibrium $Co(en)_2(hfac)^{2+} + OCH_3^- \rightleftharpoons Co(en)_2(hfacOCH_3)^+$: solvent = CH_3OH, temperature = 26 °C, $\mu = 0.5$ M ($NaClO_4$), optical path length = 1 cm, [Co(III)] = 0.005 M. 1, $[NaOCH_3] = 0.005$ M; 2, [TEAHCl] = 0.228 M, [TEA] = 0.023 M; 3, without additive.

Equilibrium Constant

The optical density of the complex at 370 nm was measured in TEA + TEAHCl buffer and the concentration ratio of the two forms of the complex was estimated ([Co(III)] = 0.0004 ~ 0.0009 M). The [TEA] and $[TEAH^+]$ were calculated from the charge balance equation. The thermodynamic equilibrium constant of reaction (1) was estimated by

$$pK_{OMe} = -6.3 + \log \frac{[TEA][CoL_4(hfac)^{n+}]}{[TEAH^+][CoL_4(hfacOCH_3)^{n-1}]} + \log \frac{\gamma(TEA)\gamma(CoL_4(hfac)^{n+})}{\gamma(TEAH^+)\gamma(CoL_4(hfacOCH_3)^{n-1})}$$

where γ(TEA) etc. denote the activity coefficient of TEA etc. The dissociation constant of TEA in methanol $pK_b = 6.3$ was used and the activity coefficient was estimated by the Debye–Hückel limiting law [3]

$$\log \gamma(i) = -1.9Z(i)^2 \sqrt{\mu} \text{ at } 25\ ^\circ C$$

where $Z(i)$ and μ denote the charge number of i species and the ionic strength. The results are summarized in Table IV. For comparison, the equilibrium constant K_{OH} for

$$CoL_4(hfac)^{n+} + OH^- \rightleftharpoons CoL_4(hfacOH)^{n-1} \quad (2)$$

in water is also given.

It should be noticed that when the charge number (Z_a) of the complex in acidic medium is 2, K_{OMe} is considerably (50 ~ 400 fold) larger than the corresponding K_{OH}.

In the case of the i-dtma complex ($Z_a = 1$), K_{OMe} is of the same order of magnitude as K_{OH}. By contrast, in the case of the edda complex ($Z_a = 0$), K_{OMe} is comparable to or even smaller than the corresponding K_{OH}. These features can be partly understood by the change ΔG_{el} in the electrostric-

TABLE IV. Thermodynamic Equilibrium Constant for Reactions (1) and (2)

Complex	$10^{-6} \times K_{OMe}$ at 26 °C (μ/M)	$10^{-6} \times K_{OH}$[a] at *ca.* 25 °C
$Co(en)_2(hfac)^{2+}$	370 (0.047)	4.2
$Co(NH_3)_4(hfac)^{2+}$	390 (0.048)	7.1
α-Co(trien)(hfac)$^{2+}$	660 (0.047)	6.5
β-Co(trien)(hfac)$^{2+}$	1260 (0.047)	3.2
f(N)-Co(i-dtma)(hfac)$^{+}$	9.0 (0.042)	1.4
α-Co(edda)(hfac)	0.10 (0.025)	0.09
β-Co(edda)(hfac)	0.18 (0.025)	0.83

[a] Estimated from the conditional constant at $\mu \leq 0.012$ M [2].

tive solvation free energy of the complex during reactions (1) and (2).

According to the Drude–Nernst equation

$$\Delta G_{el} = A(2Z_a - 1)(1 - \frac{1}{\epsilon})$$

where A is a positive number inversely proportional to the ionic radius and ϵ is the dielectric constant of the medium [4]. When Z_a is 2, the ΔG_{el} in methanol ($\epsilon = 32.6$) will be lower than that in water ($\epsilon = 78.5$). This will favor the larger K_{OMe} compared to the corresponding K_{OH}. In the case of $Z_a = 1$, a similar but lower contribution of ΔG_{el} can be expected. On the other hand, in the case of $Z_a = 0$, the contribution of ΔG_{el} will favor the smaller K_{OMe} compared to the corresponding K_{OH}. These expectations are in line with the obtained results.

Crystal Structure Determination

The structure consists of discrete β-Co(trien)-$(hfacOCH_3)^+$ cations and ClO_4^- anions. The system of numbering of the atoms in the cation is shown in Fig. 2. Figure 3 is a stereo view of the cation. The coordination polyhedron has a slightly distorted octahedral geometry (see bond lengths and angles in Table II). The 'bite' angles of the trien ligand are less than 90° (average 86.3°) while the 'bite' angle of the β-diketone ring is 94.8°. The interatomic distances and angles within the trien ligand are normal [5]. The bond lengths within the β-diketone chelate ring however deviate significantly from the normal values as a result of the sp^3 hybridization of C(4) due to the addition of $-OCH_3$ to C(4). The O(2)–C(4) and C(3)–C(4) bond lengths (1.35 and 1.50 Å respectively) are significantly longer than the normal C–O and C–C bond lengths in the β-diketone ligand [6, 7]. The C(4)–O(41) bond distance (1.44 Å) is about the same as the C–O (oxygen atom of –OH group) bond distance in $Co(en)_2(hfacOH)^+$ [1]. The chelate ring also deviates significantly from the normal planar geometry as a result of the sp^3 hybridization, see Fig. 3.

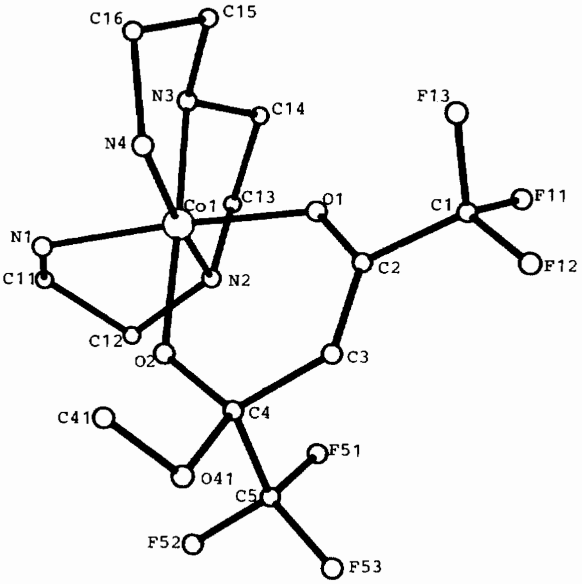

Fig. 2. Perspective view of the β-Co(trien)$(hfacOCH_3)^+$ ion.

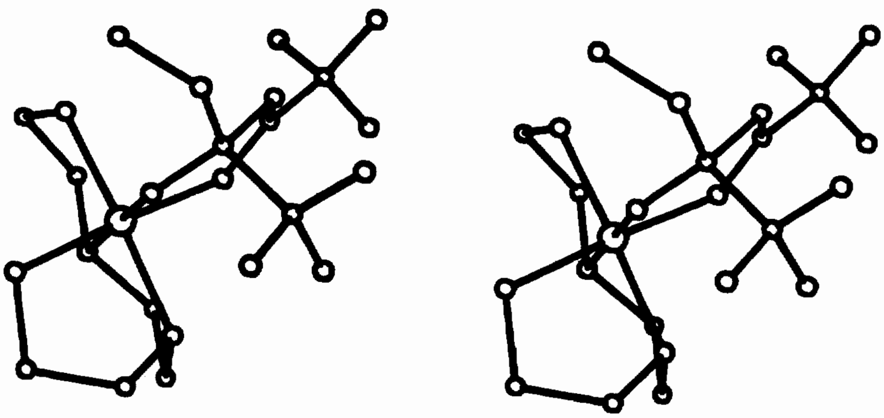

Fig. 3. Stereoview of the β-Co(trien)$(hfacOCH_3)^+$ ion.

The bond lengths and angles within the ClO_4^- ion are normal [5]. There are however some disorders in this part of the molecule as can be seen from the relatively large temperature coefficients of O(11), O(12), O(13) and O(14).

Supplementary Material

The thermal parameters as well as a listing of the observed and calculated structure factors may be obtained from the authors on request.

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