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Crystal structure of [Co(en)$_2$(hfacOCH$_3$)]ClO$_4$

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Abstract

[Co(en)$_2$(hfacOCH$_3$)]ClO$_4$ was synthesized by means of the reaction between Co(en)$_2$(hfac)$^{2+}$ and OCH$_3^-$ in a methanolic medium. It crystallized in the monoclinic space group $P2_1/c$ with $a = 7.918(1)$, $b = 14.971(2)$, $c = 15.980(2)$ Å, $\beta = 98.422(8)°$ and $Z = 4$. The structure was determined from 3357 observed reflections. The final R value converged to 0.067. Hhfac = hexafluoroacetylacetone.

Introduction

We have recently studied a pH dependent reversible color change in aqueous or methanolic solution of cobalt(III) complex CoL(hfac)$^{n+}$ with the bidentate hexafluoroacetylacetonate (hfac) ligand, where L ligand occupies the residual four coordination sites [1–3]. We have interpreted that this phenomenon is caused by a reversible lyate anion addition to one of the carbonyl carbon atoms of the hfac ligand. We intended to confirm our interpretation by a crystallographic analysis of the lyate anion added species. We have already analysed single crystals of [Co(en)$_2$(hfacOH)]Br·H$_2$O and β-[Co(trien)-(hfacOCH$_3$)]ClO$_4$ (en = ethylenediamine, trien = 1,8-diamino-3,6-diazaoctane) [2, 3]. In the present work, we have prepared a single crystal of [Co(en)$_2$(hfacOCH$_3$)]ClO$_4$ and analysed its structure. This study could be additional evidence for the above mentioned interpretation.

Experimental

[Co(en)$_2$(hfacOCH$_3$)]ClO$_4$ was synthesized by means of the reaction between Co(en)$_2$(hfac)$^{2+}$ and OCH$_3^-$ in a methanolic medium. [Co(en)$_2$(hfac)](ClO$_4$)$_2$ was dissolved in methanol. A slight excess of a methanolic solution of NaOCH$_3$ and a small amount of NaClO$_4$ were added successively to this solution. After some time [Co(en)$_2$(hfacOCH$_3$)]ClO$_4$ crystallized from this solution.

The reddish-violet compound [(Co(en)$_2$(hfac-OCH$_3$)]ClO$_4$, C$_{10}$H$_{20}$N$_4$O$_7$ClCoF$_6$) molecular weight 516.6 crystallizes in the monoclinic space group $P2_1/c$ with $a = 7.918(1)$, $b = 14.971(2)$, $c = 15.980(2)$ Å, $\beta = 98.422(8)°$, $Z = 4$, $D_{exp} = 1.82$ and $D_{calc} = 1.77$ g cm^{-3}. The three dimensional intensity data were collected for θ values between 3 and 27° on a Enraf-Nonius CAD4F diffractometer using graphite monochromated Mo Kα radiation. A crystal with dimensions $0.15 \times 0.15 \times 0.075$ mm was used for the data collection. No decomposition of the crystal was detected during the data collection. A total of 4376 reflections was measured of which 3357 were considered as observed ($I > 3\sigma(I)$). The data were corrected for Lorentz, polarization and absorption effects.

The structure was solved by Patterson and Fourier methods. The final R value converged to 0.067 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 1. The interatomic bond distances and bond angles are given in Table 2.

Results and discussion

The unit cell contains discrete Co(en)$_2$-(hfacOCH$_3$)$^+$ cations and ClO$_4^-$ anions. This

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TABLE 1. Positional ($\times 10^4$) and thermal parameters ($\times 10^3$) for $[Co(en)_2(hfacOCH_3)]ClO_4$

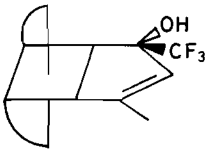
Atom	*x*	*y*	*z*	U_{eq}[a]
Co	6549(1)	5315.9(5)	2720.8(5)	61.1(6)
O(1)	5350(6)	6146(3)	3292(3)	81(3)
O(2)	4940(6)	5287(3)	1732(3)	79(3)
N(1)	5293(7)	4367(3)	3196(3)	78(3)
N(2)	7824(7)	4450(3)	2142(3)	78(3)
N(3)	7840(7)	6240(3)	2209(3)	83(3)
N(4)	8150(6)	5270(3)	3789(3)	72(3)
Cl(1)	8668(2)	8361(1)	1060(1)	83(1)
C(1)	4302(8)	6780(4)	2829(4)	71(3)
C(2)	3503(8)	6649(4)	2020(4)	71(3)
C(3)	3881(8)	5961(4)	1545(4)	71(3)
C(4)	2872(9)	6863(4)	3473(4)	80(4)
F(41)	1911(7)	6125(3)	3438(3)	145(4)
F(42)	1764(6)	7526(3)	3243(3)	129(3)
F(43)	3428(6)	7000(3)	4287(2)	128(3)
C(5)	3047(9)	5905(5)	640(4)	90(4)
F(51)	2185(7)	5129(3)	489(3)	140(3)
F(52)	1919(6)	6545(3)	405(3)	133(3)
F(53)	4161(6)	5919(4)	104(3)	135(5)
O(11)	7152(7)	7863(4)	1029(4)	139(4)
O(22)	9237(9)	8351(5)	252(4)	165(5)
O(33)	9988(7)	7993(4)	1662(4)	136(4)
O(44)	8380(8)	9266(3)	1277(4)	137(4)
C(11)	6326(11)	4015(5)	3992(5)	116(5)
C(41)	7282(10)	4778(5)	4416(4)	99(4)
C(21)	9227(9)	4922(5)	1716(5)	103(4)
C(31)	8532(11)	5835(5)	1473(5)	113(5)
O(5)	5086(6)	7672(3)	2944(3)	99(3)
O(6)	6426(12)	7888(6)	3658(6)	135(6)

[a] $U_{eq} = \frac{1}{3}\Sigma_i \Sigma_j [U_{ij}(a^*_i a^*_j)(\mathbf{a}_i \cdot \mathbf{a}_j)]$.

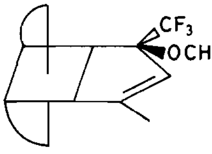
TABLE 2. Selected interatomic distances (Å) and bond angles (°) for $[Co(en)_2(hfacOCH_3)]ClO_4$

Bond	Distance (Å)	Bond	Distance (Å)
Co–O(1)	1.879(5)	C(21)–C(31)	1.52(1)
Co–O(2)	1.880(4)	C(1)–C(2)	1.509(8)
Co–N(1)	1.951(5)	C(1)–O(5)	1.471(7)
Co–N(2)	1.957(5)	C(1)–C(4)	1.53(1)
Co–N(3)	1.968(6)	C(2)–C(3)	1.338(9)
Co–N(4)	1.972(5)	C(3)–C(5)	1.502(8)
O(1)–C(1)	1.336(7)	C(4)–F(41)	1.338(8)
O(2)–C(3)	1.318(7)	C(4)–F(42)	1.339(8)
N(1)–C(11)	1.504(9)	C(4)–F(43)	1.328(7)
N(2)–C(21)	1.52(1)	C(5)–F(51)	1.351(9)
N(3)–C(31)	1.50(1)	C(5)–F(52)	1.326(9)
N(4)–C(41)	1.491(9)	C(5)–F(53)	1.312(9)
C(11)–C(41)	1.48(1)	C(6)–O(5)	1.48(1)
Angle	(°)	Angle	(°)
O(1)–Co–O(2)	95.4(2)	C(1)–C(2)–C(3)	123.2(5)
N(1)–Co–N(4)	86.4(2)	Co–N(1)–C(41)	79.5(3)
N(2)–Co–N(3)	86.2(2)	N(1)–C(11)–C(41)	107.2(6)
Co–O(1)–C(1)	125.8(4)	C(2)–O(5)–C(6)	152.0(5)
Co–O(2)–C(3)	120.2(4)	O(1)–C(1)–C(2)	118.2(5)
O(1)–Co–N(2)	179.1(2)	O(1)–C(1)–C(4)	106.0(5)
O(2)–Co–N(4)	175.8(2)	O(2)–C(3)–C(5)	110.5(5)
N(1)–Co–N(3)	177.8(2)	C(1)–C(4)–F(42)	114.5(5)
		C(3)–C(5)–F(53)	112.6(6)

cation has a Λ*R*,Δ*S* diastereoisomeric structure, whereas the cation in $[Co(en)_2(hfacOH)]Br \cdot H_2O$ has a Λ*S*,Δ*R* structure [1, 2].



Λ*S* form



Λ*R* form

The system of numbering of the atoms in the cation is shown in Fig. 1. The coordination polyhedron has a slightly distorted octahedral geometry (see bond lengths and angles in Table 2). The 'bite' angles of the ethylenediamine ligands are less than 90° (average 86.3°) whilst the bite angle of the *β*-diketone ring is 95.4°. The bond lengths and angles within the two ethylenediamine ligands are normal. The interatomic distances and angles within the *β*-diketone chelate ring however deviate significantly from the normal values as a result of the sp^3 hybridization of C(1) due to the addition of $-OCH_3$ to C(1).

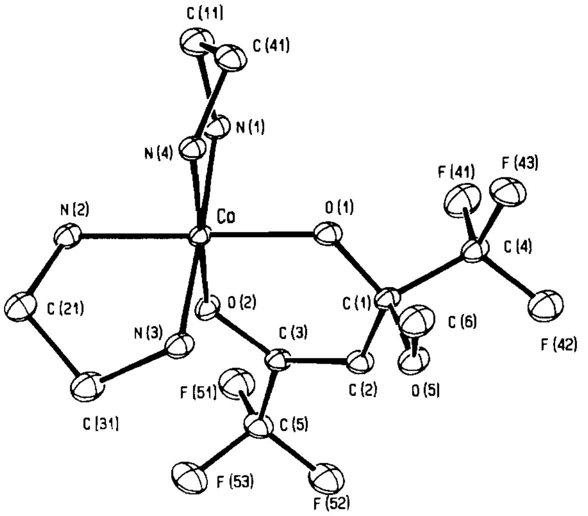


Fig. 1. Perspective view of the $Co(en)_2(hfacOCH_3)^+$ ion showing also the system of numbering of the atoms in the ion.

The O(1)–C(1) and C(1)–C(2) bond lengths (1.336 and 1.509 Å, respectively) are significantly longer than the normal O–C and C–C bond lengths in the *β*-diketone ligand [4, 5] but compare favourably with the O–C and C–C bond lengths in *β*-

$Co(trien)(hfacOCH_3)^+$ [3] and $Co(en)_2(hfacOH)^+$ [2]. The C(1)–O(5) bond distance (1.471 Å) is about the same as the C–O bond distances in β-$Co(trien)(hfacOCH_3)^+$ [3] (oxygen atom of the $-OCH_3$ group) and in $Co(en)_2(hfacOH)^+$ [2] (oxygen atom of the –OH group). The chelate ring also deviates significantly from the normal planar geometry as a result of the sp^3 hybridization of C(1). The bond lengths and angles within ClO_4^- are considered normal.

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.

Acknowledgements

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