Synthesis and Characterization of the Thermally Stable Ho(hfa)₃(tme)

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Holmium β-diketonate complexes, Ho(hfa)₃(tme), has been prepared and characterized by IR, TGA, MS, and single-crystal X-ray analyses. This complex is air- and moisture-stable and most importantly has good volatility and thermal stability. Holmium atom binds to nine oxygen atoms, contributed by six oxygen atoms of three hfa ligands and three oxygen atoms of the tme ligand. The coordination polyhedron of Ho can be described as a distorted tricapped trigonal prism. Crystal data for Ho(hfa)₃(tme): orthorhombic P2₁2₁2₁, a = 15.415(4), b = 13.17(2), c = 17.291(3) Å, V = 3496(1) Å³.

Key Words : Holmium, Tricapped trigonal prism, hfa, CVD, 9-Coordination

Introduction

Metal β-diketonates find extensive use in chemical vapour deposition (CVD) process, which involve the formation of thin film for optical or microelectronic applications by CVD. The conventional lanthanide precursors for such films have several drawbacks, mostly notably in the high residue left in commercial evaporators and poor stability to the atmosphere.[1-3] A considerable diversity of β-diketonates and Lewis bases has been used to improve such properties. We have described the synthesis and characterization of Lanthanide (β-diketonate)₃(polyether) complex. The reactions of linear-polyether with the hydrated lanthanide β-diketonate complexes yielded the water-free lanthanide β-diketonate complexes showing thermal stability.[4-6] In this paper we report the reaction of branched-polyether (tme) with the hydrated holmium β-diketonate complex and discuss the structural characterization and thermal stability of Ho(hfa)₃-(tme).

Experimental Section

General procedures. All manipulations were performed under an inert atmosphere using Schlenk techniques. All solvents were distilled by standard techniques. Holmium oxide, Hhfa, MeI, NaH, and Triol were purchased from Aldrich and used as received.[7] Ho(hfa)₃(H₂O)₂ was prepared as previously described. FAB mass spectra were determined using a JOEL SX-102 spectrometer with 3-nitrobenzyl alcohol as the matrix material. Infrared spectra were recorded as KBr pellets on a Shimadzu FTIR-8501 model. TGA analysis was carried out on a SETARAM TGA-92 instrument.

Preparation of 1,1,1-tris(methoxymethyl)ethane (tme). The triol (1.0 g, 8.15 mmol) was dissolved in 100 mL of THF. Sodium hydride (0.28 g, 8.2 mmol) was added, and then the mixture was refluxed for 1d. 3-Methoxypropyl iodide (2.15 g, 10.1 mmol) dissolved in THF was added to the suspension, and the reaction mixture was refluxed for 1d. The product mixture was distilled to give pure 1,1,1-

tris(methoxymethyl)ethane.[8] Yield: 0.65 g (49%), bp 152-154 °C.

Preparation of Ho(hfa)₃(tme). Method 1. To a Schlenk flask containing Ho₂O₃ (0.20 g, 0.529 mmol) and tme (0.172 g, 1.06 mmol) were added 20 mL of toluene and Hhfa (0.45 mL, 3.18 mmol). After stirring and refluxing for 2d the remaining holmium oxide was filtered off. The solvent was removed *in vacuo* to yield yellow precipitates. Slow evaporation of hot dilute hexane solution gave crystals suitable for x-ray crystallography. Yield: 0.58 g, 58 °C.

Method 2. To a benzene solution (10 mL) of Ho(hfa)₃-(H₂O)₂ (0.22 g, 0.268 mmol) was added tme (0.043 g, 0.268 mmol). After stirring and refluxing for 1d the volume of solution was reduced to half. Yield: 0.21 g, 83%, mp: 112-116 °C. IR (KBr, cm⁻¹): 3380 (w), 2920 (w), 1640 (s), 1540 (m), 1510 (m), 1480 (s), 1410 (w), 1340 (w), 1240 (s), 1190

Table 1. Crystal Data and Structure Refinement for Ho(hfa)₃(tme)

formula	$C_{23} H_{21} F_{18} Ho O_9$
fw	948.33
T (°C)	20(2)
wavelength, Å	0.71070
space group	P2₁2₁2₁
a, Å	15.415(4)
b, Å	13.117(2)
c, Å	17.291(3)
V, Å³	3496.2(12)
Z	4
ρ_{calcd}, g cm⁻³	1.802
μ(Mo Kα), cm⁻¹	24.02
no. of rflns colletd	3555
no. of indep rflns	3058 [R(int)=0.0166]
no. of params	457
GOF on F²	1.055
final R indices [I > 2σ(I)]	R1 = 0.0452, wR2 = 0.1269
R indices (all data)	R1 = 0.0566, wR2 = 0.1402
largest diff. peak and hole, eÅ³	+1.031 and -1.009

[a]$R1 = \Sigma|F_0| - |F_c| / \Sigma|F_0|$, wR2 = $\{\Sigma w(F_0^2 - F_c^2)^2 / \Sigma w F_0^4\}^{1/2}$, where $w = 1/\{\sigma^2 F_0^2 + (0.0786P)^2 + 5.28P\}$ and where $p = \{Max(F_0^2, 0) - 2F_c^2\}/3$

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Ho(hfa)₃-(tme)

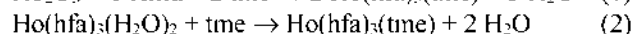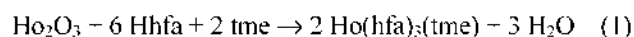| Ho-O(1)	2.341(9)	Ho-O(2)	2.42(2)
Ho-O(3)	2.378(9)	Ho-O(4)	2.273(13)
Ho-O(5)	2.338(12)	Ho-O(6)	2.390(8
Ho-O(7)	2.376(12)	Ho-O(8)	2.502(11)
Ho-O(9)	2.458(7)	O(1)-C(2)	1.26(2)
O(2)-C(4)	1.19(2)	O(3)-C(7)	1.26(2)
O(4)-C(9)	1.28(2)	O(5)-C(12)	1.25(2)
O(6)-C(14)	1.28(2)	O(7)-C(18)	1.45(2)
O(7)-C(19)	1.44(2)	O(8)-C(20)	1.41(3)
O(8)-C(21)	1.41(2)	O(9)-C(22)	1.39(2)
O(9)-C(23)	1.42(2)	C(1)-C(2)	1.64(3)
C(2)-C(3)	1.35(3)	C(3)-C(4)	1.37(2)
C(4)-C(5A)	1.26(4)	C(5)-C(5A)	1.53(7)
C(6)-C(6A)	0.9(2)	C(6)-C(7)	1.6(2)
C(6A)-C(7)	1.47(4)	C(7)-C(8)	1.37(2)
C(8)-C(9)	1.39(3)	C(9)-C(10)	1.75(4)
C(11)-C(12)	1.54(3)	C(12)-C(13)	1.39(2)
C(13)-C(14)	1.40(3)	C(14)-C(15)	1.47(2)
C(16)-C(17)	1.56(2)	C(16)-C(18)	1.55(4)
C(16)-C(20)	1.38(4)	C(16)-C(22)	1.48(2)
O(1)-Ho-O(2)	69.8(4)	O(1)-Ho-O(3)	71.4(4)
O(1)-Ho-O(4)	73.6(4)	O(1)-Ho-O(5)	73.9(4)
O(1)-Ho-O(6)	132.9(3)	O(1)-Ho-O(7)	142.4(4)
O(1)-Ho-O(8)	138.4(4)	O(1)-Ho-O(9)	94.5(3)
O(2)-Ho-O(3)	120.3(4)	O(2)-Ho-O(4)	133.3(5)
O(2)-Ho-O(5)	69.2(5)	O(2)-Ho-O(6)	126.3(5)
O(2)-Ho-O(7)	72.7(4)	O(2)-Ho-O(8)	133.5(5)
O(2)-Ho-O(9)	69.1(6)	O(3)-Ho-O(4)	71.8(4)
O(3)-Ho-O(5)	136.3(4)	O(3)-Ho-O(6)	113.4(5)
O(3)-Ho-O(7)	129.3(4)	O(3)-Ho-O(8)	67.0(4)
O(3)-Ho-O(9)	70.7(5)	O(4)-Ho-O(5)	73.5(3)
O(4)-Ho-O(6)	65.1(4)	O(4)-Ho-O(7)	138.1(5)
O(4)-Ho-O(8)	93.2(5)	O(4)-Ho-O(9)	142.5(6)
O(5)-Ho-O(6)	73.6(4)	O(5)-Ho-O(7)	94.3(4)
O(5)-Ho-O(8)	140.9(5)	O(5)-Ho-O(9)	138.2(6)
O(6)-Ho-O(7)	73.0(4)	O(6)-Ho-O(8)	67.5(5)
O(6)-Ho-O(9)	132.2(3)	O(7)-Ho-O(8)	71.0(4)
O(7)-Ho-O(9)	70.5(5)	O(8)-Ho-O(9)	72.0(5)
C(2)-O(1)-Ho	133.4(10)	C(4)-O(2)-Ho	134.8(12)
C(7)-O(3)-Ho	135.4(11)	C(9)-O(4)-Ho	134.3(11)
C(12)-O(5)-Ho	135.9(12)	C(14)-O(6)-Ho	128.3(11)
C(18)-O(7)-Ho	130.1(12)	C(19)-O(7)-Ho	115.7(9)
C(20)-O(8)-Ho	126(2)	C(21)-O(8)-Ho	122.0(12)
C(22)-O(9)-Ho	127.9(8)	C(23)-O(9)-Ho	118.4(8)

(s), 1130 (s), 1080 (m), 1060 (w), 800 (w), 655 (w). MS (FAB; m/z (fragment)): 885 (P-tme-CF₃CH₃tfa), 732 (P-tme+CF₃+CH₃), 671 (P-tme-hfa+2CH₃OCH₃), 553 (P-tme-hfa), 529 (P-tme-hfa-CF₂).

X-ray crystal analysis. Crystallographic parameters and information related to data collection and structural refinements for the complex are given in Table 1. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the empirical φ-scan method. The structure were solved by the Patterson method (SHELXS-86) and were refined by full-matrix least squares techniques (SHELXL-93). All non-hydrogen atoms were refined anisotropically and the positions of hydrogen atoms were idealized, assigned isotropic thermal parameters [U_{iso}(H) = 1.2 U_{eq}(C)] and allowed to ride on the parent carbon atoms. All calculations were carried out on the personal computer with use of the SHELXS-86 and SHELXL-93 programs.[9,10] Selected bond lengths and angles are given in Table 2.

Results and Discussion

Preparation. Ho(hfa)₃(tme) complex has been synthesized from two different pathways summarized by (1) and (2). Ho(hfa)₃(tme) was obtained by the reaction of Ho₂O₃ with Hhfa and tme in toluene (1). In addition this compound was also synthesized from the reaction of Ho(hfa)₃(H₂O)₂ with tme ligand (2).

$$Ho_2O_3 - 6\ Hhfa + 2\ tme \rightarrow 2\ Ho(hfa)_3(tme) - 3\ H_2O \quad (1)$$
$$Ho(hfa)_3(H_2O)_2 + tme \rightarrow Ho(hfa)_3(tme) + 2\ H_2O \quad (2)$$

This compound has a low melting point of 112-116 °C and sublimes intact. More importantly, this compound displays excellent stability to both moisture and oxygen, with negligible decomposition over a period of months in the open laboratory. We have studied for the reaction of Ho(hfa)₃-(H₂O)₂ with several polyether ligands.

$$Ho(hfa)_3(H_2O)_2 + polyether\ (monoglyme,\ diglyme,\ tme)$$
$$\longrightarrow Ho(hfa)_3(polyether) + 2\ H_2O$$
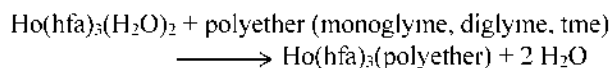
The reactions of Ho(hfa)₃(H₂O)₂ with monoglyme, diglyme, and tme ligand yield polyether-coordinated holmium complexes. The polyether ligand acts as a partitioning agent, removing the coordinated water completely.
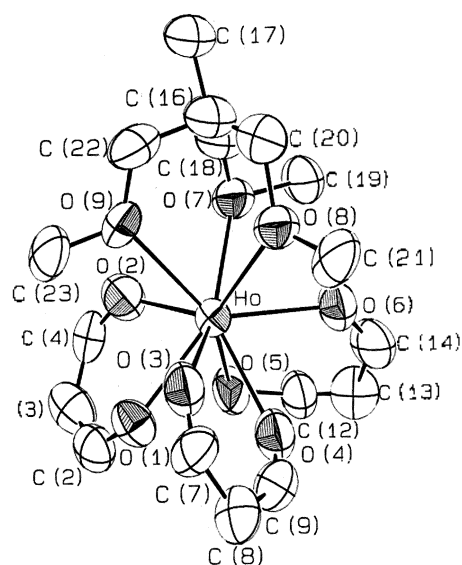

Figure 1. ORTEP drawing of the crystal structure of Ho(hfa)₃(tme) showing the atomic labelling scheme and thermal ellipsoidal at 50% level.
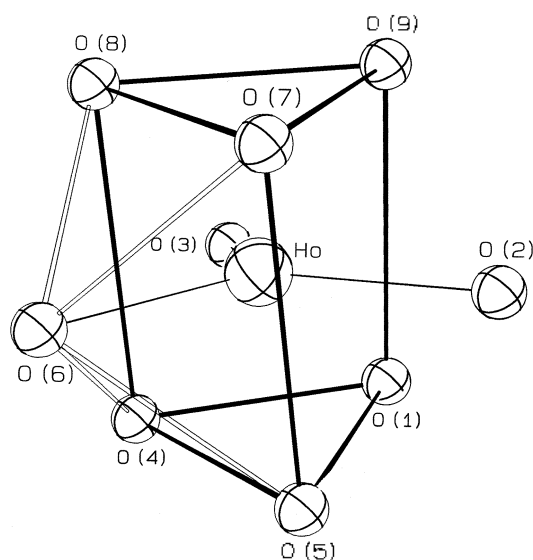
Figure 2. Coordination polyhedron of Ho(hfa)₃(tme) showing the Ho environment.

Structural description of Ho(hfa)₃(tme). The molecular structure of Ho(hfa)₃(tme) is shown in Figure 1, with the CF_3 groups of hfa ligand have been omitted for clarity. Holmium atom binds to nine oxygen atoms, contributed by six oxygen atoms of three hfa ligands and three oxygen atoms of the tme ligand.

The two possible ground-state geometries for nine-coordination polyhedra are the tricapped trigonal prism with D_{3h} symmetry and the monocapped square antiprism with C_{4v} symmetry.[11-13] The coordination polyhedron of Ho can be described as a distorted tricapped trigonal prism, with the top represented by [O(7), O(8), O(9)] plane, the bottom depicted by the [O(1), O(4), O(5)], and the face capped by [O(2), O(3), O(6)] (see Figure 2).

The Ho-O bond length of Ho(hfa)₃(tme) can be classified by three group; one from neutral tme ligand and two from anionic hfa ligands. The average Ho-O bond distance of hfa ligands (2.36[2] Å) is shorter than that of the tme ligand (2.45[1] Å) (Table 2). As mentioned, the Ho-O bond length of hfa ligands falls into two distinctly different groups; those formed the trigonal plane (average 2.32[1] Å) and those capped the prismatic faces (average 2.40[1] Å). The coordination number and the size of the central metal affect the bond length of the metal-coordinated atom. The average Ho-O (of hfa) bond length for the nine coordinated Ho(hfa)₃·tme [2.36 Å] is longer than that for the eight coordinated Ho(hfa)₃·monoglyme [2.31 Å] (Table 3). The average Ln-O (of hfa) bond distance (Ln = La, Eu, Ho) is in the order of La-O > Eu-O > Ho-O. These differences are in part due to the significantly different ionic radii of the metal centers involved. The polyhedron geometry of Ho(hfa)₃·tme is a distorted tricapped trigonal prism while La(hfa)₃·diglyme and Eu(hfa)₃·diglyme adapted a capped square antiprism. This geometric difference might be due to the role of polyether. The linear diglyme polyether gives the capped square antiprism while a branched tme forms the tricapped

Table 3. The Average Lengths of Ln-O(of hfa), Coordination Number and Geometry for the Ln-O(of hfa)(polyether) Complexes

Comp.	Average lengths of Ln-O(of hfa)	Coordination number	Geometry
Ho(hfa)₃·monoglyme	2.31[1]	8	sq. an.*
Ho(hfa)₃·tme	2.36[1]	9	cap. tri. pr.
La(hfa)₃·diglyme	2.53[1]	9	cap. sq. an.
Eu(hfa)₃·diglyme	2.40[1]	9	cap. sq. an.

*sq. an.: square antiprism. cap. tri. pr.: tricapped trigonal prism. cap. sq. an.: capped square antiprism

Table 4. Bond Separation [Å] and Angles [deg] for Ho(hfa)₃(tme)

O(1)--O(4)	2.76	O(1)--O(5)	2.81
O(1)--O(9)	3.52	O(4)--O(5)	2.76
O(4)--O(8)	3.47	O(5)--O(7)	3.46
O(7)--O(8)	2.83	O(7)--O(9)	2.79
O(8)--O(9)	2.91	O(4)--O(7)	4.34
O(5)--O(8)	4.56	O(2)--O(3)	4.16
O(2)--O(6)	4.29	O(3)--O(6)	3.99
O(4)--O(6)	2.51	O(5)--O(6)	2.83
O(7)--O(6)	2.84	O(8)--O(6)	2.72
O(1)-O(4)-O(5)	61.2	O(1)-O(5)-O(4)	59.4
O(4)-O(1)-O(5)	59.4	O(7)-O(8)-O(9)	58.9
O(7)-O(9)-O(8)	59.5	O(8)-O(7)-O(9)	61.6
O(4)-O(5)-O(7)	87.7	O(4)-O(8)-O(7)	86.5
O(5)-O(4)-O(8)	93.4	O(5)-O(7)-O(8)	92.4
O(1)-O(9)-O(7)	87.7	O(1)-O(9)-O(8)	86.5
O(9)-O(1)-O(4)	93.4	O(9)-O(1)-O(5)	92.4

trigonal prism.

The average O-Ho-O angle of the same hfa ligand is 71.7[2]° and the corresponding angle of the tme ligand is 71.1[5]°. The average O-Ho-O angle among capping oxygen atoms, e.g. O(2)-Ho-O(3), is 120[1]° whereas that locating oxygen atoms in a trigonal plane, e.g. O(1)-Ho-O(4), is 73.7[3]°.

The average O--O separation in trigonal planes, e.g. O(1)--O(5), is 2.81 Å while that among capping oxygen atoms, e.g. O(2)--O(3), is 4.15 Å (Table 4). The length of rectangle is about 2.81 × 3.48 Å. The mean plane separation between two trigonal planes is about 3.48 Å and two trigonal planes are nearly parallel. There are two type's dihedral angles, one between squares planes and the other between square and trigonal plane. The former, e.g. O(1)-O(5)-O(7)-O(9) and O(4)-O(5)-O(7)-O(8), is close to 60 and the latter, e.g. O(1)-O(5)-O(7)-O(9) and O(7)-O(8)-O(9), is nearly orthogonal.

The average C-O distance of hfa ligands is 1.25[2] Å whereas the corresponding bond length of the tme is 1.42[3] Å. The C-C bond distances of the hfa ligands fall into two distinctly different groups; C(1)-C(2) and C(4)-C(5), 1.51[2] Å and C(2)-C(3) and C(3)-C(4), 1.39[2] Å. The average C-C bond distances of the tme ligand is about 1.50[2] Å. There are intra (CH--O) and inter (CH--F) molecular hydrogen bonds.

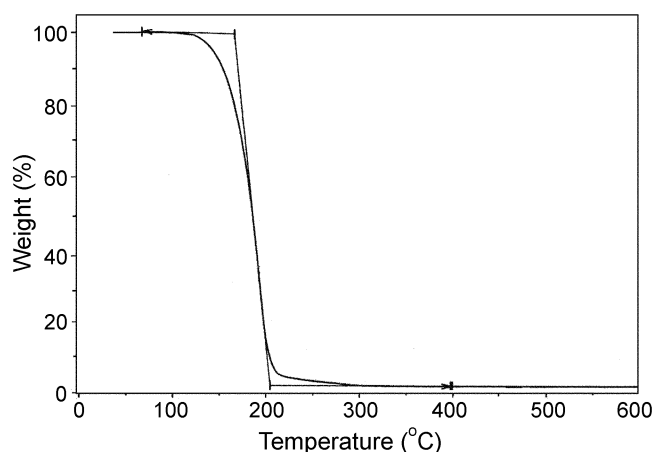**Other properties.** To evaluate the utility of Ho(hfa)₃(tme)

Figure 3. TGA diagram of Ho(hfa)₃(tme).

as precursors for CVD, the thermogravic behavior of the complexes has been investigated by TGA over the temperature range 30-600 °C. The TGA curve of Ho(hfa)₃(tme) is reported in Figure 3. The TGA plot shows a singular sublimation step in the 110-210 °C temperature range and no weight loss after 290 °C.

This indicates that Ho(hfa)₃(tme) is a stable potential precursor which delivers the homoleptic tme complex into the gas phase easily. A final residue of 1.56% indicates an almost quantitative sublimation. This might be attributed to the highly electronegative CF₃ group of the hfa ligand and therefore no loss of the tme during TGA experiment. IR spectra of Ho(hfa)₃(tme) show characteristic bands for the β-diketonate with strong absorption bands for carbonyl group at 1640 cm⁻¹. The C-F stretching frequencies of hfa ligand fall in the same regions as those of the C-O for the tme. In the MS spectrum of Ho(hfa)₃(tme), prominent signals correspond to the fragments (P-tme-hfa), (P-tme-hfa-CF₂), (P-tme-CF₃+CH₃-tfa), (P-tme+CF₃+CH₃), (P-tme-hfa+ 2CH₃OCH₃). Molecular ion peak is not observed.

Conclusions

The thermally stable Ho(hfa)₃(tme) complex was readily synthesized from the reaction of Ho(hfa)₃(H₂O)₂ with tme.

The product has been shown to be air- and moisture-stable with sublime intact. The X-ray structural characterization of Ho(hfa)₃(tme) shows that holmium metal ion is saturated with nine coordinates. The polyhedron geometry of Ho(hfa)₃(tme) is a distorted tricapped trigonal prism while La(hfa)₃-diglyme and Eu(hfa)₃-diglyme adapted a capped square antiprism. This geometric difference might be due to the role of polyether.

Supporting Information Available. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data centre (Deposition No. CCDC-241715). The data can be obtained free of charge via *www.ccdc.cam.ac.uk/conts/retrieving.html* (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax:-441223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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7. Abbreviations used in this paper include: Hhfa. hexafluoroacetylacetone; hfa. anion of Hhfa: Triol. 2-(hydroxymethyl)-2-methyl-1,3-propanediol or 1,1,1-tris(hydroxymethyl)ethane: tme. 1,1,1-Tris(methoxymethyl)ethane. 4-Methoxymethyl-4-methyl-2,6-dioxaheptane
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