Synthesis and Characterization of Holmium Complexes Containing β-Diketonate Ligands

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Two holmium β-diketonate complexes, $Ho(hfa)_3(H_2O)_2$ (**1**) and $[Ho(hfa)_3(H_2O)_2]$(triglyme) (**2**), have been prepared and characterized by IR, TGA, and single-crystal X-ray analyses. These complexes show polymeric chains by the intermolecular hydrogen bondings. The donor atoms of the intermolecular hydrogen bonding in both complexes are hydrogen atoms of the coordinated water molecules. The acceptor atoms in **1** are the carbonyl oxygen atoms of β-diketonate ligands whereas those in **2** are oxygen atoms of the triglyme ligand. While compound **1** decomposes cleanly to Ho_2O_3, compound **2** sublimes intact. Crystal data for **1** and **2** are as follows: $Ho(hfa)_3(H_2O)_2$ triclinic $P\bar{1}$, a=10.158(4), b=11.628(2), c=12.579(6) Å, α= 67.02(3)°, β=73.95(4)°, γ= 76.12(2)°, V=1299.8(8) Å^3. $[Ho(hfa)_3(H_2O)_2]$(triglyme), monoclinic $P2_1/c$, a=12.559(3), b=19.111(2), c= 16.789(6) Å, β=110.59(4)°, V=3772(2) Å^3.

Introduction

There is a considerable interest in the development of chemical vapour deposition (CVD) process for the deposition of thin films of high-Tc superconducting materials.[1] This requires the availability of suitable precursors with sufficient volatility and thermal stability. In general the hydrous CVD precursors, however, have the low volatility and thermal instability by the intermolecular interaction.[2] These low volatility and thermal instability can be overcome by the saturation of the metal coordination sphere using neutral polyether ligands. This Lewis base, polyether, saturates the metal coordination sphere, thus maintaining monomeric character and thereby increasing vapour pressure and volatility.[3] In this paper, we report the synthesis and characterization of two hydrous holmium complexes. An interesting aspect of **2** is the thermal stability and volatility even though the presence of intermolecular hydrogen bonding.

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, and triglyme were purchased from Aldrich and used as received.[4] Infrared spectra were recorded as KBr pellets on a Shimadzu FTIR-8501 model. TGA/DTA analyses were carried out on a SETARAM TGA-92 instrument, which simultaneously performs thermogravimetry (TGA) and differential thermal analysis (DTA). The weight of the samples was between 10 and 25 mg. The measurements were performed in alumina crucibles under an atmosphere of flowing dry nitrogen, using heating rates of 5 °C/min from ambient temperature up to 500 °C.

Preparation of $Ho(hfa)_3(H_2O)_2$, 1. To a suspension of Ho_2O_3 (0.5 g, 1.32 mmol) in 50 mL of benzene were added Hhfa (1.13 mL, 7.94 mmol) and H_2O (0.2 mL, 13 mmol) under nitrogen atmosphere. The resulting mixture was refluxed for 3 h. On cooling to room temperature, the remaining holmium oxide was filtered off and the resulting yellow solution was removed in vacuo to yield crystalline powders. Slow evaporation of dilute benzene solution gave yellow crystals suitable for X-ray crystallography. Yield: 2.05 g, 95%. mp 124-130 °C. IR (KBr, cm^{-1}): 3400 (m), 1651 (s), 1562 (m), 1539 (m), 1504 (s), 1474 (w), 1258 (s), 1225 (s), 1200 (s), 1156 (s), 1144 (s), 1101 (m).

Preparation of $[Ho(hfa)_3(H_2O)_2]$(triglyme), 2. Method 1. To a toluene solution of $Ho(hfa)_3(H_2O)_2$ (0.2 g, 0.243 mmol) was added triglyme (0.044 mL, 0.243 mmol). After stirring for 2 h, the solution was filtered and volume of the filtrate was reduced to half. Slow evaporation of this solution gave yellow crystals suitable for X-ray crystallography. Yield: 0.22 g, 92%. mp 69-71 °C. Anal. Calc. for $C_{23}H_{25}O_{12}F_{18}Ho$: C, 27.62; H, 2.5. Found: C, 27.63; H, 2.3. IR (KBr, cm^{-1}): 3360 (m), 3240 (m), 2920 (w), 1655 (s), 1550 (m), 1528 (m), 1500 (s), 1475 (m), 1255 (s), 1205 (s), 1140 (s), 1095 (s), 1012 (w), 935 (w), 840 (w). Method 2. To a suspension of Ho_2O_3 (1.0 g, 2.65 mmol) in toluene (150 mL) were added Hhfa (2.24 mL, 15.88 mmol) and triglyme (0.95 mL, 5.29 mmol). The mixture was refluxed for 2 d. On cooling to ambient temperature, the remaining holmium oxide was filtered off and the resulting yellow solution was removed in vacuo to yield oily product. To the oily product were added 2 mL of methyl alcohol and 20 mL of water. The yellow precipitates were formed and washed with cold benzene. Slow evaporation of benzene solution gave yellow crystals suitable for X-ray crystallography. Yield: 2.97 g, 56%.

X-ray crystal analysis. Crystallographic parameters and information related to data collection and structural refinements for the complexes are given in Table 1. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected for by the empirical φ-scan method.[5] The structure were solved by the Patterson method (SHELXS-86) and were refined by full-matrix least squares

Table 1. Crystal data and structure refinement for $Ho(hfa)_3(H_2O)_2$ and $[Ho(hfa)_3(H_2O)_2](triglyme)$

	$Ho(hfa)_3(H_2O)_2$	$[Ho(hfa)_3(H_2O)_2]$ (triglyme)
Formula	$C_{15}H_7F_{18}HoO_8$	$C_{23}H_{25}F_{18}HoO_{12}$
Fw	822.14	1000.36
T(°C)	20	20
Wavelength, Å	0.71073	0.71073
Space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a, Å	10.158(4)	12.559(3)
b, Å	11.628(2)	19.111(6)
c, Å	12.579(6)	16.789(6)
α, deg	67.02(3)	
β, deg	73.95(4)	110.59(4)
γ, deg	76.12(2)	
V, Å^3	1299.8(8)	3772(2)
Z	2	4
ρ_{calcd}, gcm^{-3}	2.101	1.761
μ(Mo Kα), cm^{-1}	32.10	22.37
No. of rflns collctd	3319	4842
No. of indep rflns	3108 [R(int)=0.0205]	4627 [R(int)=0.0239]
No. of params	407	501
GOF on F^2	1.069	1.052
Final R indices [$I>2\sigma(I)$]	$R1$[a]=0.0405, $wR2$=0.1077	$R1$[a]=0.0465, $wR2$=0.1211
R indices (all data)	$R1$=0.0407, $wR2$=0.1080	$R1$=0.0478, $wR2$=0.1224
Largest diff. peak and hole, eÅ^{-3}	+0.918 and −0.924	+1.097 and −1.778

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

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.[6] Selected bond lengths and angles are given in Table 2 and Table 3.

Results and Discussion

Preparation. $Ho(hfa)_3(H_2O)_2$ was obtained by the reaction of Ho_2O_3 with Hhfa in benzene. The product was isolated as a pale-yellow powder. As expected, the yield of this reaction is dependent on the reaction condition, mainly on the presence of water. In the presence of water, $Ho(hfa)_3(H_2O)_2$ was obtained in quantitative yield. This compound can be a good precursor for the syntheses of various Ho derivatives due to a good solubility in common organic solvents such as alcohol, benzene, toluene, and chloroform.

$$Ho_2O_3 + 6Hhfa + H_2O \rightarrow 2Ho(hfa)_3(H_2O)_2$$

In general the reactions of polyether with the hydrated lanthanide β-diketonate complexes have been reported to produce the water-free lanthanide β-diketonate complexes.[7] The polyether ligand acts as a partitioning agent, removing

Table 2. Selected bond lengths [Å] and angles [deg] for $Ho(hfa)_3(H_2O)_2$

Ho-O(1)	2.366(6)	Ho-O(2)	2.364(6)
Ho-O(3)	2.349(6)	Ho-O(4)	2.281(6)
Ho-O(5)	2.343(6)	Ho-O(6)	2.323(6)
Ho-O(7)	2.374(7)	Ho-O(8)	2.344(7)
O(1)-C(2)	1.249(11)	O(2)-C(4)	1.235(11)
O(3)-C(7)	1.258(11)	O(4)-C(9)	1.232(11)
O(5)-C(12)	1.270(11)	O(6)-C(14)	1.247(11)
O(1)-Ho-O(2)	71.9(2)	O(1)-Ho-O(3)	69.0(2)
O(1)-Ho-O(4)	110.7(2)	O(1)-Ho-O(5)	150.8(2)
O(1)-Ho-O(6)	135.0(2)	O(1)-Ho-O(7)	80.6(3)
O(1)-Ho-O(8)	82.3(2)	O(2)-Ho-O(3)	113.4(2)
O(2)-Ho-O(4)	73.4(2)	O(2)-Ho-O(5)	84.7(2)
O(2)-Ho-O(6)	147.4(2)	O(2)-Ho-O(7)	73.5(3)
O(2)-Ho-O(8)	138.9(2)	O(3)-Ho-O(4)	73.0(2)
O(3)-Ho-O(5)	138.5(2)	O(3)-Ho-O(6)	72.5(2)
O(3)-Ho-O(7)	143.5(2)	O(3)-Ho-O(8)	84.8(2)
O(4)-Ho-O(5)	77.6(2)	O(4)-Ho-O(6)	78.4(2)
O(4)-Ho-O(7)	139.2(2)	O(4)-Ho-O(8)	147.1(2)
O(5)-Ho-O(6)	73.3(2)	O(5)-Ho-O(7)	76.1(2)
O(5)-Ho-O(8)	106.1(2)	O(6)-Ho-O(7)	122.0(3)
O(6)-Ho-O(8)	71.9(2)	O(7)-Ho-O(8)	71.1(2)
C(2)-O(1)-Ho	129.9(6)	C(4)-O(2)-Ho	130.2(6)
C(7)-O(3)-Ho	132.8(6)	C(9)-O(4)-Ho	135.3(6)
C(12)-O(5)-Ho	130.4(6)	C(14)-O(6)-Ho	133.0(6)

Table 3. Selected bond lengths [Å] and angles [deg] for $[Ho(hfa)_3(H_2O)_2](triglyme)$

Ho-O(1)	2.329(5)	Ho-O(2)	2.360(6)
Ho-O(3)	2.320(6)	Ho-O(4)	2.350(6)
Ho-O(5)	2.291(6)	Ho-O(6)	2.366(6)
Ho-O(7)	2.320(6)	Ho-O(8)	2.344(6)
O(1)-C(2)	1.251(9)	O(2)-C(4)	1.241(10)
O(3)-C(7)	1.243(12)	O(4)-C(9)	1.244(10)
O(5)-C(12)	1.272(12)	O(6)-C(14)	1.243(11)
O(9)-C(16)	1.38(2)	O(9)-C(17)	1.47(2)
O(10)-C(18)	1.39(2)	O(10)-C(19)	1.431(14)
O(11)-C(20)	1.415(13)	O(11)-C(21)	1.431(13)
O(12)-C(22)	1.415(13)	O(12)-C(23)	1.40(2)
O(1)-Ho-O(2)	73.5(2)	O(1)-Ho-O(3)	78.9(2)
O(1)-Ho-O(4)	136.8(2)	O(1)-Ho-O(5)	78.3(2)
O(1)-Ho-O(6)	120.9(2)	O(1)-Ho-O(7)	145.0(2)
O(1)-Ho-O(8)	69.2(2)	O(2)-Ho-O(3)	72.8(2)
O(2)-Ho-O(4)	124.5(2)	O(2)-Ho-O(5)	75.5(2)
O(2)-Ho-O(6)	139.3(2)	O(2)-Ho-O(7)	73.2(2)
O(2)-Ho-O(8)	140.3(2)	O(3)-Ho-O(4)	72.0(2)
O(3)-Ho-O(5)	145.0(2)	O(3)-Ho-O(6)	143.4(2)
O(3)-Ho-O(7)	101.2(2)	O(3)-Ho-O(8)	86.9(2)
O(4)-Ho-O(5)	140.6(2)	O(4)-Ho-O(6)	73.4(2)
O(4)-Ho-O(7)	73.2(2)	O(4)-Ho-O(8)	77.9(2)
O(5)-Ho-O(6)	71.6(2)	O(5)-Ho-O(7)	83.3(2)
O(5)-Ho-O(8)	108.9(3)	O(6)-Ho-O(7)	79.8(2)
O(6)-Ho-O(8)	74.4(2)	O(7)-Ho-O(8)	145.6(2)
C(2)-O(1)-Ho	133.9(5)	C(4)-O(2)-Ho	133.9(6)
C(7)-O(3)-Ho	136.2(6)	C(9)-O(4)-Ho	134.6(6)
C(12)-O(5)-Ho	137.6(7)	C(14)-O(6)-Ho	135.3(6)

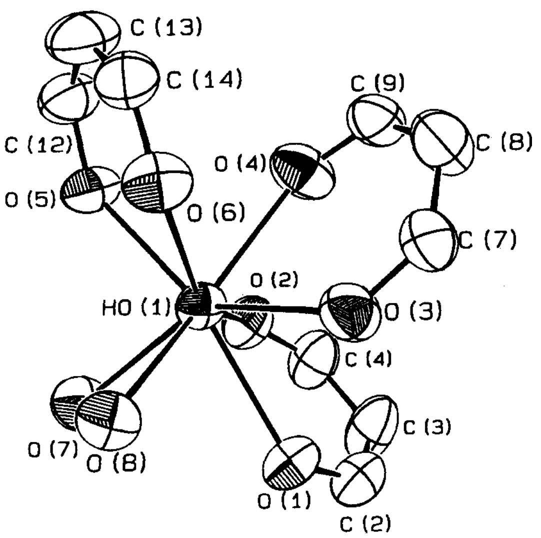

Figure 1. ORTEP drawing of the crystal structure of $Ho(hfa)_3(H_2O)_2$ showing the atomic labelling scheme and thermal ellipsoidal at 50% level.

$$Ln(\beta\text{-diketonate})_3(H_2O)_x + L \longrightarrow Ln(\beta\text{-diketonate})_3(L) + xH_2O$$
(Ln=La, Eu, Y, or Tb; L=polyether ligand)

the coordinated water. In contrast to our expectation, the reaction of $Ho(hfa)_3(H_2O)_2$ with triglyme in toluene yields $[Ho(hfa)_3(H_2O)_2]$(triglyme) which not only has water molecules coordinated to Ho atom but also holds triglyme through hydrogen bonds. The yield of this reaction is nearly quantitative. This compound was also synthesized from the reaction of holmium oxide with hexafluoroacetylacetone in the presence of triglyme. This coordination mode of the polyether ligand is quite unique; such ligands are normally found either chelating and/or bridging bonding modes.[8] The product is nonhygroscopic, can be handled in air, and is soluble in common organic solvents such as benzene, toluene, and methanol.

$$Ho(hfa)_3(H_2O)_2 + \text{triglyme} \longrightarrow [Ho(hfa)_3(H_2O)_2](\text{triglyme})$$
$$Ho_2O_3 + 6Hhfa + 2\text{triglyme} + H_2O \longrightarrow 2[Ho(hfa)_3(H_2O)_2](\text{triglyme})$$

Structural description of 1. The molecular structure of $Ho(hfa)_3(H_2O)_2$ is shown in Figure 1, with the CF_3 groups of hfa anionic ligand have been omitted for clarity. Holmium atom binds to eight oxygen atoms, contributed by three bidentate hfa ligands and two water molecules [O(7) and O(8)] resulting in a distorted square antiprism. The molecules are linked by intermolecular hydrogen bonds between hydrogen atoms of water molecules and oxygen atoms of hfa ligand, Figure 3. Each of water molecules is connected to the hfa ligand of the different $Ho(hfa)_3(H_2O)_2$ molecules [O(7)--O(2)' and O(5)'; O(8)--O(1)" and O(3)"] causing the zigzag chain running along the crystallographic z axis of the lattice. The $La(acac)_3(H_2O)_2$ molecules are also linked in chains by hydrogen bonds.[9] The closest Ho··Ho separation in the rods is 8.04 Å and no close contacts exist between the chains. The Ho-O bond distances range from 2.28 to 2.37 Å and the average C-O distance of hfa ligands is 1.25[1] 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), 1.52[2] Å and C(2)-C(3) and C(3)-C(4), 1.38[2] Å. The average O-Ho-O bite angle of the hfa ligand is 72.7[2]° and the corresponding angle of the water molecules is 71.1[2]°. The O··O distances in **1** range from 2.87 to 3.02 Å.

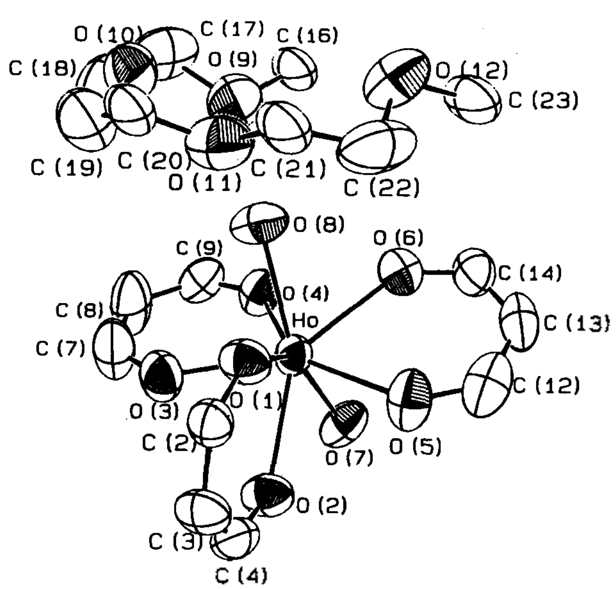

Figure 2. ORTEP drawing of the crystal structure of $[Ho(hfa)_3(H_2O)_2]$(triglyme) showing the atomic labelling scheme and thermal ellipsoidal at 50% level.

Structural description of 2. The coordination polyhedron of $[Ho(hfa)_3(H_2O)_2]$(triglyme) showing the Ho environment is shown in Figure 2. The holmium metal center is eight coordinate, with the overall coordination polyhedron being distorted square antiprism. In $[Ho(hfa)_3(H_2O)_2]$(triglyme), the triglyme ligand is not coordinated to holmium atom but is in the second sphere. The most interesting feature in this molecule is that $[Ho(hfa)_3(H_2O)_2]$(triglyme) molecules have one-dimensional networks by intermolecular hydrogen bonding interactions.

Figure 4 shows a unit cell packing diagram consisting of two parallel rods for $[Ho(hfa)_3(H_2O)_2]$(triglyme). These hydrogen-bonds, found between O(7) and O(10)/O(12), O(8) and O(9)/O(11), give chains running along the crystallographic z axis of the lattice. That is, the function of the triglyme is to provide a hydrogen-bond acceptor for the coordinated water molecules. Thus the triglyme adopts a conformation that directs O(9)/O(11) or O(10)/O(12) toward the protons of the coordinated water. In this conformation, triglyme has the appearance of a fragment of a cyclic polyether. The hydrogen bonding and the crystal lattice serve to stabilize a conformation of triglyme. The Ho-O bond distances range from 2.31 to 2.36 Å and the average C-O distance of hfa ligands is 1.25[1] 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), 1.52[2] Å and C(2)-C(3) and C(3)-C(4), 1.37[2] Å. The average O-Ho-O bite angle of the hfa ligand is 72.4[2]° and the corresponding angle of the water molecules is 145.6[2]°. The closest Ho··Ho separation in the rods is 8.73 Å and the corresponding distance between neighboring rods is 11.81 Å. It is apparent that there are no close contacts between atoms of neighboring rods. The O··O distances in **2** range from 2.71 to 2.87 Å, which is in the range normally found for hydrogen-bonded water molecules.

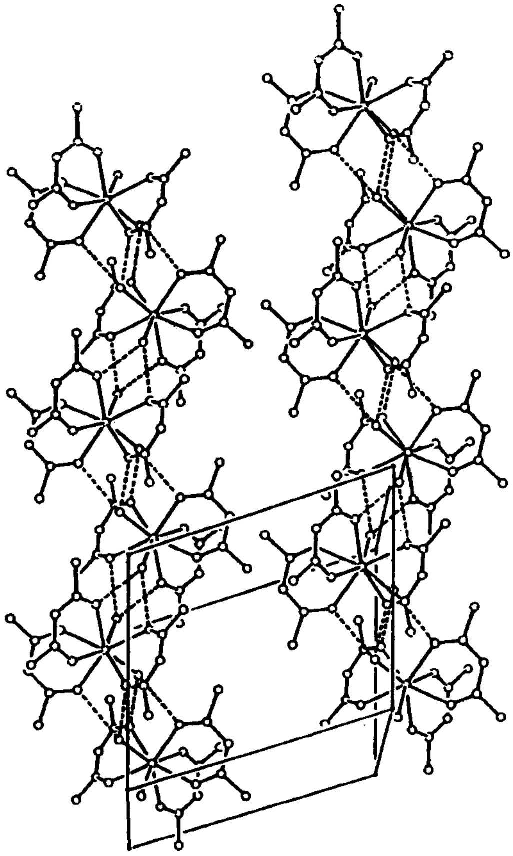

Figure 3. Unit cell packing digram of Ho(hfa)$_3$(H$_2$O)$_2$ showing the chains running along the z axis.

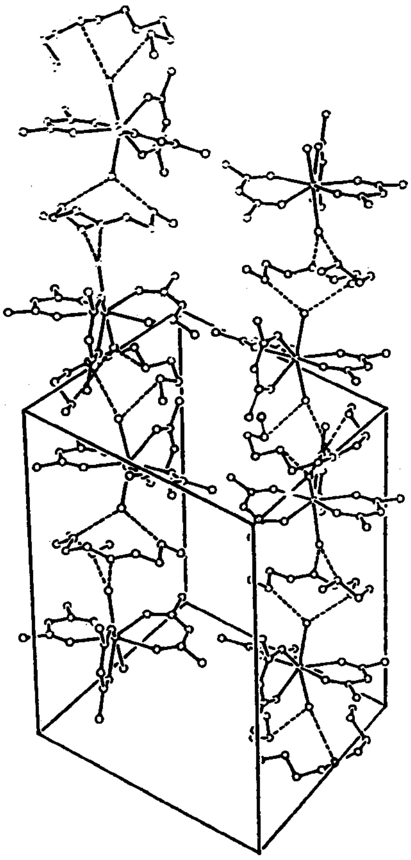

Figure 4. Unit cell packing digram of [Ho(hfa)$_3$(H$_2$O)$_2$](triglyme) showing the chains running along the z axis.

Structural comparison of complexes 1 and 2. There are several fundamental solid-state structural motifs displayed by trivalent lanthanide or pseudolanthanide β-diketonate complexes. For the anhydrous case, six-coordinated monomeric and seven-coordinated dimeric species have previously been reported.[8] For the hydrous case, seven-coordinated monomeric, seven-coordinated dimeric, eight-coordinated polymeric and nine-coordinated species have also been reported.[9] We reported here two eight-coordinated polymeric complexes; Ho(hfa)$_3$(H$_2$O)$_2$ and [Ho(hfa)$_3$(H$_2$O)$_2$](triglyme). The donor atoms of the intermolecular hydrogen bonding in both complexes are hydrogen atoms of the coordinated water molecules. The acceptor atoms in both complexes, however, are different; the carbonyl oxygen atoms of hfa ligand in complex **1** and oxygen atoms of the triglyme ligand in complex **2**. The comparison of the O-Ho-O angle of the water ligand is interesting; the O-Ho-O angle of the water ligand for Ho(hfa)$_3$(H$_2$O)$_2$ is 71.1[2]° whereas the corresponding angle for [Ho(hfa)$_3$(H$_2$O)$_2$](triglyme) is 145.6(2)°.

These angles are quite related with the linearity of the polymeric chain. The wide angle makes the polymeric chain close to linear; the Ho-Ho-Ho angle in the polymeric chain for Ho(hfa)$_3$(H$_2$O)$_2$ is 103° and the corresponding angle for [Ho(hfa)$_3$(H$_2$O)$_2$](triglyme) is 148°. Figure 4 show that [Ho(hfa)$_3$(H$_2$O)$_2$](triglyme) has the polymeric chain close to linear.

Other properties. The thermogravic behaviors of the complexes have been investigated by thermogravimetry (TGA) and differential thermal analysis (DTA) over the temperature range 20-500 ℃. Atmospheric pressure thermogravimetric analysis of **1** reveals that weight loss takes place in the 120-290 ℃ temperature range and shows that no weight loss after 300 ℃. The final residual weight (~21%) agrees well with the composition of Ho$_2$O$_3$ (~23%). Compound **2** undergoes two major stages of weight loss. The first stage occurred at about 100 ℃, resulting in approximately 3.0% weight loss, which might be attributed to

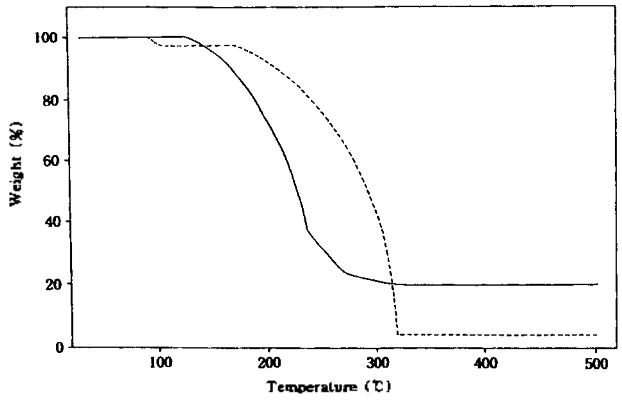

Figure 5. TGA diagram of **1** and **2**. The solid curve is for Ho(hfa)$_3$(H$_2$O)$_2$ and the dashed curve is for [Ho(hfa)$_3$(H$_2$O)$_2$](triglyme).

the loss of water (theoretical weight loss 3.6%). The second stage corresponds to the sublimation of the resulting product. Over the temperature range studied, 95±2% of **2** volatilizes into the gas phase. These data suggest that complex **2** has a good mass transport property for the CVD precursor. Furthermore, the complex **2** has a low melting point of 69-71 ℃ with respect to the starting complex, $Ho(hfa)_3(H_2O)_2$, which melts over the range 124-130 ℃.

In $Ho(hfa)_3(H_2O)_2$, prominent signals correspond to the fragments ($P-2H_2O$), ($P-2H_2O-CF_3$), ($P-2H_2O$-hfa), ($P-2H_2O$-hfa-CF_3+F), and ($P-2H_2O$+acac). Molecular peak is not observed. Fragments like ($P-2H_2O$-hfa-CF_3+F) result from fluorine transfer that occurs upon the loss of CF_3 fragment. The observation of higher-molecular-weight ions indicates that this species aggregates in the gas phase to yield dimeric species. In $[Ho(hfa)_3(H_2O)_2]$(triglyme), prominent signals correspond to the fragments ($P-2H_2O$-hfa), ($P-2H_2O$-triglyme), ($P-2H_2O$+hfa-triglyme), ($P-2H_2O$-triglyme-CF_3), and ($P-2H_2O$-2hfa+F). Rather suprising thing is the observation of the predominant mass peak corresponding to $[Ho(hfa)_2$(triglyme)] at m/z 757. The weak $[Ho(hfa)_4]$ peak was also observed at m/z 1006.

The IR spectrum of complex **1** shows characteristic bands for the β-diketonates, with strong absorption bands for carbonyl group; C=C conjugated stretch at 1565-1530; C=O conjugated stretch at 1650-1655 cm^{-1}. The IR spectrum of complex **2** shows characteristic bands at 2920 cm^{-1} for triglyme assigned as C-H stretch. The C-F stretching frequencies of hfa group fall in the same regions as those of the C-O(triglyme). The ^1H NMR spectra (C_6D_6) of complex **1** and **2** show a considerable degree of peak shifting and line broading and this is undoubtedly due to the paramagnetic Ho^{3+}.

Conclusions

Two complexes show polymeric chains by intermolecular hydrogen bondings. Triglyme ligand and $Ho(hfa)_3(H_2O)_2$ in compound **2** cocrystallizes by the intermolecular hydrogen bond whereas $Ho(hfa)_3(H_2O)_2$ in **1** is connected by itself to give intermolecular hydrogen bondings. This difference is of interest from the following points of views; 1) $[Ho(hfa)_3(H_2O)_2]$(triglyme) sublimes near completely while $Ho(hfa)_3(H_2O)_2$ decomposes to holmium oxide. 2) $[Ho(hfa)_3(H_2O)_2]$(triglyme) shows lower melting point than that of $Ho(hfa)_3(H_2O)_2$. 3) $[Ho(hfa)_3(H_2O)_2]$(triglyme) has a nearly linear polymeric chain whereas $Ho(hfa)_3(H_2O)_2$ has a zigzag chain. The triglyme ligand is believed to play an important role in terms of volatility and thermal stability.

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Supporting Information Available. Experimental details of X-ray crystal structure determination, crystallographic tables, listing of atomic coordinates, thermal parameters, and bond distances and angles.

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