Notes

Synthesis and Characterization of Thermally Stable Ln(hfa)$_3$(monoglyme) (Ln=Ho, Y, hfa=hexafluoroacetylacetone) Complexes

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Introduction

There is a considerable interest in the development of chemical vapour deposition processes for the deposition of thin films of high-temperature superconducting materials, such as $YBa_2Cu_3O_{7-x}$, $HgBa_2CaCu_2O_6$, $Bi_2Sr_2CaCu_2O_8$, $Tl_2Ba_2CaCu_2O_8$.[1] This process requires the availability of suitable precursors with sufficient volatility and thermal stability. Various types of metal β-diketonate precursors are applied for this purpose. We recently described the synthesis and characterization of the [Ho(hfa)$_3$(H_2O)$_2$](triglyme) compound.[2] In general the reactions of polyether with hydrated lanthanide β-diketonate complexes have been reported to produce water-free lanthanide β-diketonate complexes.[3] The reaction of Ho(hfa)$_3$(H_2O)$_2$ with triglyme in toluene, however, yields [Ho(hfa)$_3$(H_2O)$_2$](triglyme) adduct which not only has water molecules coordinated to Ho atom but also holds triglyme through intermolecular hydrogen bonds.[2] This observation prompted us to examine the reaction of Ho(hfa)$_3$(H_2O)$_2$ with monoglyme. In this paper we report the preparation and characterization of Ln(hfa)$_3$(monoglyme) (Ln=Ho and Y) complexes. Ho(hfa)$_3$(monoglyme) sublimes intact while Gd(tmhd)$_3$(monoglyme) loses the monoglyme ligand.[4]

Experimental Section

General procedures. All manipulations were performed under nitrogen atmosphere using Schlenk techniques. All solvents were dried by standard techniques. Holmium oxide, yttrium oxide, Hhfa, and monoglyme were purchased from Aldrich and used as received.[5] Ho(hfa)$_3$(H_2O)$_2$ and Y(hfa)$_3$(H_2O)$_2$ were prepared as previously described.[3] NMR spectra were recorded on a Bruker DPX-300 spectrometer. 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/DSC analyses were carried out on a SETARAM TGA-92 instrument, which simultaneously performs thermogravimetry (TGA) and differential scanning calorimetry (DSC).

Preparation of Ho(hfa)$_3$(monoglyme). Method 1. To a suspension of Ho_2O_3 (0.20 g, 0.529 mmol) in 50mL of toluene in a Schlenk flask were added Hhfa (0.45 mL, 3.18 mmol) and monoglyme (0.11 g, 1.058 mmol) with stirring under nitrogen. The mixture was heated to reflux with stirring for 2d. After cooling to ambient temperature the remaining holmium oxide was filtered off and the solvent was removed in vacuo to yield yellow precipitates. Cooling hot hexane solution to ambient temperature gave crystals suitable for X-ray crystallography. Yield: 0.50 g, 52%. Method 2. To a benzene solution (10 mL) of Ho(hfa)$_3$(H_2O)$_2$ (0.2 g, 0.243 mmol) was added monoglyme (0.022 g, 0.243 mmol). The mixture was heated to reflux with stirring for 1d. The solvent was removed in vacuo to yield yellow precipitates. Slow evaporation of the benzene solution gave crystals suitable for X-ray crystallography. Yield: 0.20 g, 90%. mp: 76-77 °C.

IR (KBr, cm^{-1}): 2940 (w), 1640 (s), 1610 w), 1560 (m), 1530 (m), 1495 (m), 1350 (w), 1260 (s), 1250 (s), 1210 (s), 1140 (s), 1100 (m), 1045 (m), 1020 (w), 870 (m), 835 (w), 800 (m), 770 (w), 745 (w), 660 (m). MS (FAB) [m/z (fragment)]: 885 (P-monoglyme-CF_3+CH_3+tfa), 732 (P-monoglyme-CF_3+CH_3), 579 (P-monoglyme-hfa), 529 (P-monoglyme-hfa-CF_2).

Preparation of Y(hfa)$_3$(monoglyme). To a benzene (20 mL) solution of Y(hfa)$_3$(H_2O)$_2$ (0.18 g, 0.243 mmol) was added monoglyme (0.022 g, 0.243 mmol). After refluxing for 1d, gravimetric impurity was filtered off and the resulting solvent was removed *in vacuo* to yield an oily product. Washing with hexane produced white precipitates. Cooling of hot hexane solution gave crystals suitable for X-ray crystallography. Yield: 0.15 g, 70%. mp: 75-76 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 6.19 (s, 3H, CH of hfa), 2.96 (s, 6H, OCH_3), 2.60 (s, 4H, OCH_2). MS (FAB) [m/z (fragment)]: 809 (P-monoglyme-CF_3+CH_3+tfa), 656 (P-monoglyme-CF_3+CH_3), 503 (P-monoglyme-hfa), 453 (P-monoglyme-hfa-CF_2).

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 by the empirical φ-scan method.[6] 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 aniso-

Table 1. Crystal Data and Structure Refinement for $Ho(hfa)_3$ (monoglyme)

formula	$C_{19}H_{13}F_{18}HoO_8$
fw	876.22
T (°C)	20
wavelength, Å	0.71070
space group	*Pbca* (No. 61)
a, Å	20.762(2)
b, Å	17.946(3)
c, Å	16.075(4)
V, 3 Å	5990(2)
Z	8
ρ_{calcd}, gcm^{-3}	1.943
μ (Mo Kα), cm^{-1}	27.93
no. of indep rflns	4651
no. of params	417
GOF on F^2	1.088
final R indices [$I > 2\sigma(I)$]	R1[a] =0.0572, wR2=0.1471
R indices (all data)	R1=0.1123, wR2=0.2057
largest diff. peak and hole, e $Å^{-3}$	+1.781 and 1.011

[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 $p=\{\text{Max}(F_o^2,0)+2F_c^2\}/3$.

ropically 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.[7] Selected bond lengths and angles are given in Table 2.

Results and Discussion

Preparation. The preparation of $Ln(hfa)_3$(monoglyme) (Ln=Y and Ho) can be accomplished from two different pathways summarized by eq. 1 and 2. $Ln(hfa)_3$(monoglyme) was obtained by the reaction of Ln_2O_3 with Hhfa and monoglyme in toluene (eq. 1). This compound was alternatively synthesized from the reaction of $Ln(hfa)_3(H_2O)_2$ with monoglyme ligand (eq. 2).

$$Ln_2O_3 + 6Hhfa + 2monoglyme \rightarrow 2Ln(hfa)_3(monoglyme) + 3H_2O \quad (1)$$

$$Ln(hfa)_3(H_2O)_2 + monoglyme \rightarrow Ln(hfa)_3(monoglyme) + 2H_2O \quad (2)$$

Ln = Ho and Y

The complexes have a low melting point of 75-77 °C and sublime intact. More importantly, these complexes display excellent stability to both moisture and oxygen, with negligible decomposition over a period of months in the open laboratory. As mentioned before, the reaction of $Ho(hfa)_3(H_2O)_2$ with triglyme yields the hydrated $[Ho(hfa)_3(H_2O)_2]$(triglyme). The reaction of $Ho(hfa)_3(H_2O)_2$ with monoglyme, however, gives the anhydrous $Ho(hfa)_3$(monoglyme). This is, we believe, mainly due to the sterically bulky triglyme ligand.

$$Ho(hfa)_3(H_2O)_2 + triglyme \rightarrow [Ho(hfa)_3(H_2O)_2](triglyme)$$

Table 2. Selected Bond Lengths [Å] and Angles [deg] for $Ho(hfa)_3$(monoglyme)

Ho-O(1)	2.326(7)	Ho-O(2)	2.310(8)
Ho-O(3)	2.300(9)	Ho-O(4)	2.308(7)
Ho-O(5)	2.300(9)	Ho-O(6)	2.309(9)
Ho-O(7)	2.442(10)	Ho-O(8)	2.428(12)
O(1)-C(2)	1.222(11)	O(2)-C(4)	1.238(12)
O(3)-C(7)	1.23(2)	O(4)-C(9)	1.233(13)
O(5)-C(12)	1.21(2)	O(6)-C(14)	1.262(14)
O(7)-C(16)	1.37(2)	O(7)-C(17)	1.44(3)
O(8)-C(18)	1.45(2)	O(8)-C(19)	1.42(2)
C(1)-C(2)	1.49(2)	C(2)-C(3)	1.41(2)
C(3)-C(4)	1.37(2)	C(4)-C(5)	1.49(2)
C(6)-C(7)	1.55(2)	C(7)-C(8)	1.39(2)
C(8)-C(9)	1.36(2)	C(9)-C(10)	1.51(2)
C(11)-C(12)	1.51(2)	C(12)-C(13)	1.38(2)
C(13)-C(14)	1.36(2)	C(14)-C(15)	1.53(2)
C(17)-C(18)	1.36(3)		
O(1)-Ho-O(2)	72.7(3)	O(1)-Ho-O(3)	148.2(3)
O(1)-Ho-O(4)	138.5(3)	O(1)-Ho-O(5)	75.7(3)
O(1)-Ho-O(6)	78.5(3)	O(1)-Ho-O(7)	112.0(4)
O(1)-Ho-O(8)	72.6(3)	O(2)-Ho-O(3)	81.3(3)
O(2)-Ho-O(4)	145.5(3)	O(2)-Ho-O(5)	140.3(3)
O(2)-Ho-O(6)	77.7(3)	O(2)-Ho-O(7)	72.8(3)
O(2)-Ho-O(8)	109.9(4)	O(3)-Ho-O(4)	72.2(3)
O(3)-Ho-O(5)	117.3(3)	O(3)-Ho-O(6)	78.3(3)
O(3)-Ho-O(7)	76.1(5)	O(3)-Ho-O(8)	135.1(3)
O(4)-Ho-O(5)	73.2(3)	O(4)-Ho-O(6)	116.7(3)
O(4)-Ho-O(7)	79.6(3)	O(4)-Ho-O(8)	76.6(3)
O(5)-Ho-O(6)	72.9(3)	O(5)-Ho-O(7)	142.9(4)
O(5)-Ho-O(8)	82.3(4)	O(6)-Ho-O(7)	143.3(4)
O(6)-Ho-O(8)	145.8(4)	O(7)-Ho-O(8)	67.0(5)
C(2)-O(1)-Ho	134.9(7)	C(4)-O(2)-Ho	133.9(7)
C(7)-O(3)-Ho	135.2(8)	C(9)-O(4)-Ho	136.3(8)
C(12)-O(5)-Ho	132.5(9)	C(14)-O(6)-Ho	131.5(8)
C(16)-O(7)-Ho	126.9(13)	C(17)-O(7)-Ho	117(2)
C(18)-O(8)-Ho	111.2(12)	C(19)-O(8)-Ho	123.3(14)
C(1)-C(2)-C(3)	117.5(10)	C(2)-C(3)-C(4)	121.0(10)
C(3)-C(4)-C(5)	115.9(12)	C(6)-C(7)-C(8)	114.3(14)
C(7)-C(8)-C(9)	121.6(11)	C(8)-C(9)-C(10)	117.3(11)

$$Ho(hfa)_3(H_2O)_2 + monoglyme \rightarrow Ho(hfa)_3(monoglyme) + 2H_2O$$

Structural Description of $Ho(hfa)_3$(monoglyme). The molecular structure of $Ho(hfa)_3$(monoglyme) is shown in Figure 1, with the CF_3 groups of the hfa anionic ligand omitted for clarity. Holmium atom binds to eight oxygen atoms, contributed by three bidentate hfa ligands and one monoglyme ligand, resulting in a distorted square antiprism. This structural type is common in holmium β-diketonate compounds; $[Ho(hfa)_3(H_2O)_2]$(triglyme), $[Ho(hfa)_3(H_2O)_2]$, and $[Ho(tmhd)_3(4\text{-pic})_2]$.[8] The Ho-O bond distances of $Ho(hfa)_3$(monoglyme) range from 2.30 to 2.44 Å. These Ho-O bond distances fall into two distinctly different groups: those to the hfa ligand which lie in the range of 2.300(9)-2.326(7) Å (average 2.308 Å) and those for the monoglyme which are 2.428(12) and 2.442(10) Å (average 2.435 Å).

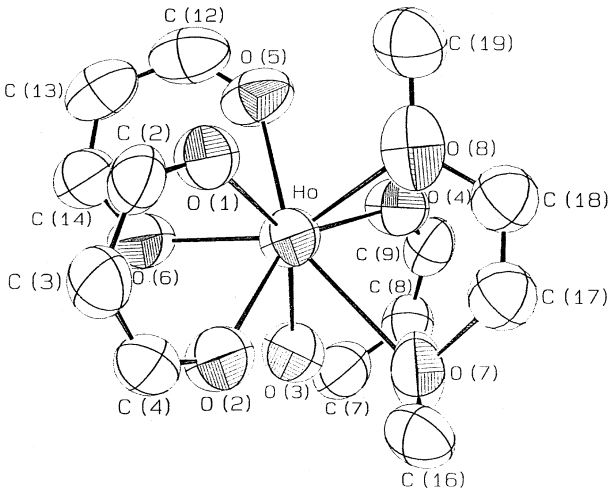

Figure 1. ORTEP drawing of the crystal structure of $Ho(hfa)_3$ (monoglyme) showing the atomic labelling scheme and thermal ellipsoidal at 50% level.

In comparison with $Gd(tmhd)_3$(monoglyme), the Ho-O_{ether} bonds (average 2.435 Å) of the $Ho(hfa)_3$(monoglyme) are relatively stronger than the Gd-O_{ether} bonds (average 2.575 Å) of the $Gd(tmhd)_3$(monoglyme).[4] The electron-withdrawing CF_3 substituents of the hfa ligand may cause the Ho- O_{ether} bonds strong. The average C-O distance of hfa ligands is 1.23[2] Å while the corresponding bond length of the monoglyme 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), 1.38[2] Å. The average O-Ho-O bite angle of the hfa ligand is 72.6[2]° and the corresponding angle of the monoglyme ligand is 67.0[5]°. The mean plane separation between two squares [O(1)-O(4)-O(5)-O(8) and O(2)-O(3)-O(6)-O(7)] is about 2.54 Å and two squares are nearly parallel which the angle between two squares is about 1.0°. The two oxygens of each hfa and monoglyme ligand are attached to the opposite top and bottom vertices of the prism. Unit cell determination of $Y(hfa)_3$(monoglyme) showed the same cell parameters with $Ho(hfa)_3$(monoglyme).

Other Properties. To evaluate the utility of $Ln(hfa)_3$ (monoglyme) as precursors for MOCVD, the thermogravic behavior of the complexes has been investigated by TGA and DSC over the temperature range 30-600 °C. The TGA curve of $Ho(hfa)_3$(monoglyme) is shown in Figure 2. The TGA plot shows a singular sublimation step in the 90-190 °C temperature range and no weight loss after 200 °C.

This indicates that $Ho(hfa)_3$(monoglyme) is a stable potential precursor which sublimes easily. The absence of the intermolecular interactions explains why this compound is so volatile. A final residue of 2.0% indicates an almost quantitative sublimation. In comparison with $Gd(tmhd)_3$ (monoglyme), a TGA curve of $Gd(tmhd)_3$(monoglyme) shows a loss of the monoglyme ligand while $Ho(hfa)_3$ (monoglyme) sublimes intact as shown below. This is in concert with our observation of Ln-O_{ether} bond strength; the average Ho-O_{ether} distance of 2.435 Å and the average Gd-O_{ether} distance of 2.575 Å.

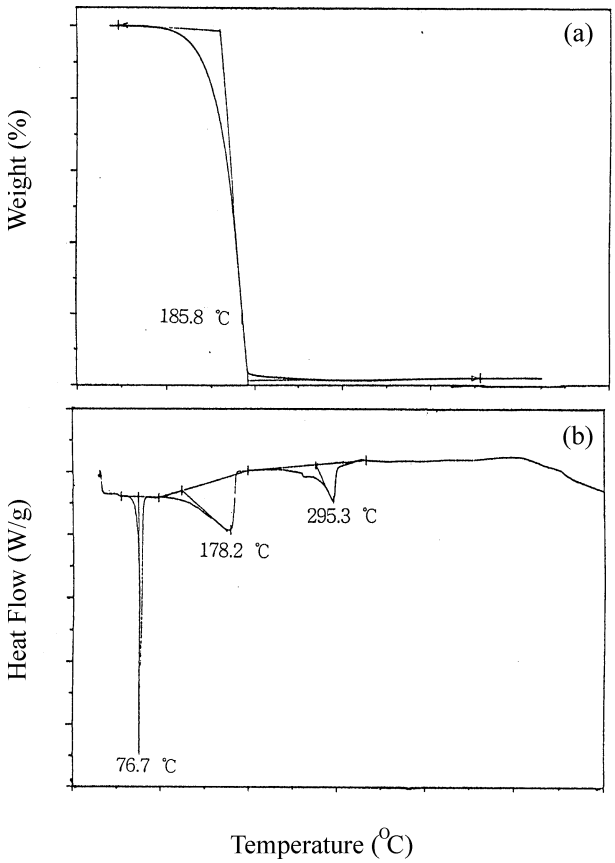

Figure 2. TGA/DSC diagram of $Ho(hfa)_3$(monoglyme). (a) TGA (b) DSC.

$Ho(hfa)_3$(monoglyme) → one-step sublimation
$Gd(tmhd)_3$(monoglyme) → $Gd(tmhd)_3$ → sublimation

Monoglyme ligand binds to the holmium metal center more tightly than to the gadolinium metal center. This might be attributed to the highly electronegative CF_3 group of the hfa ligand and thus no loss of the monoglyme during TGA experiment has been observed. The DSC curve of Ho $(hfa)_3$(monoglyme) shows a melting point endotherm at 77 °C and two other changes, at 178 °C and at 295 °C. The endothermic peak at 178 °C is presumably attributed to the sublimation. The TGA/DSC curve of the $Y(hfa)_3$(monoglyme) shows a similar pattern that of the $Ho(hfa)_3$(monoglyme); singular sublimation step in the 90-180 temperature range and no weight loss after 220 °C. IR spectra of $Ln(hfa)_3$(monoglyme) show characteristic bands for the β-diketonate with a strong absorption band for the carbonyl group at 1610 cm^{-1}. The C-F stretching frequencies of hfa ligand fall in the same regions as those of the C-O for the monoglyme. The ^1H NMR spectrum of $Y(hfa)_3$(monoglyme) in C_6D_6 at room temperature reveals only one hfa and monoglyme ligand environment. These data therefore suggest that in solution the molecule is highly fluxional with rapid exchanges among hfa and monoglyme coordination sites. In the MS spectrum of $Ho(hfa)_3$(monoglyme), promi-

nent peaks correspond to the fragments (P-monoglyme-hfa), (P-monoglyme-hfa-CF_3+F), (P-monoglyme-CF_3+CH_3+tfa), (P-monoglyme-CF_3+CH_3). Molecular ion peak is not observed. Fragments like (P-monoglyme-hfa-CF_3+F) result from the fluorine transfer that occurs upon a loss of the CF_3 fragment.

Conclusions

The thermally stable Ln(hfa)$_3$(monoglyme) complexes were readily synthesized from the reaction of Ln(hfa)$_3$(H_2O)$_2$ with monoglyme. While Gd(tmhd)$_3$(monoglyme) shows the weight loss of monoglyme, the TGA data for Ho(hfa)$_3$(monoglyme) show no weight loss. This observation is consistent with X-ray crystal structure data that the strength of binding of the monoglyme ligand to the metal center increases in the order of Ln(hfa)$_3$ moiety>Ln(tmhd)$_3$ moiety. These trends will give the idea to prepare the thermally stable lanthanide MOCVD precursors.

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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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5. Abbreviations used in this paper include: Hhfa, hexafluoroacetylacetone; hfa, anion of Hhfa; tmhd, anion of 2,2,6,6-tetramethyl-3,5-heptanedione; tha, trifluoroacetylacetone; monoglyme, ethylene glycol dimethyl ether; P, parent ion.
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