this work has been supported by the Korea Science and Engineering Foundations (KOSEF 961-0301-001-2)

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Synthesis and Characterization of [Ho(hfa)$_3$(H$_2$O)$_2$]·triglyme; Molecular Assembly of the Potential Rare-Earth CVD Precursor

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Received November 27, 1996

Efficient, reproducible metalloorganic chemical vapor deposition (MOCVD) processes hinge critically upon the availability of high-purity metalloorganic precursors with high and stable vapor pressure. Minimizing molecular oligomerization by saturating the metal coordination sphere with sterically encumbered nonpolar and/or fluorinated anionic ligands is an attractive approach.[1] The β-diketonate ligand class provides an efficacious embodiment of these strategies as initially suggested by the existence of volatile β-diketonate complexes of nearly every metal ion.[2] Although the β-diketonates have been successfully utilized as MOCVD precursors, significant deficiencies still exist with respect to vapor pressure and vapor pressure stabilities. This is especially true for the rare-earth and alkaline earth complexes.[3] The general strategy associated with the synthesis of new stable water-free and volatile rare-earth metal precursors pointed toward the saturation of the metal coordination sphere using neutral polyether ligands.[4] These Lewis base effects appear to reflect saturation of the metal coordination spheres, thus maintaining monomeric character and thereby increasing precursor vapor pressure and stability.

The single-step reaction of lanthanide oxide with hexafluoroacetylacetone and polyether in benzene has been found to yield reproducible anhydrous, air-stable adducts.[5]

$$1/2\mathrm{Ln_2O_3} + 3\mathrm{Hhfa} + \mathrm{L} \rightarrow \mathrm{Ln(hfa)_3}\cdot\mathrm{L} + 3/2\mathrm{H_2O}$$
$$\mathrm{Ln} = \mathrm{La\ and\ Eu};\ \mathrm{L} = \mathrm{diglyme\ and\ triglyme}$$

We have extended this synthetic method to the late rare-earth metal oxide for the preparation of MOCVD precursors. We herein describe the synthesis, structural characterization and sublimation properties of [Ho(hfa)$_3$(H$_2$O)$_2$]·triglyme.[6,7]

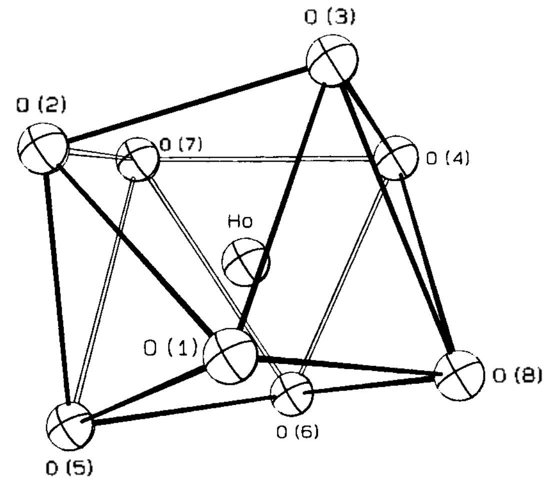

Figure 1. Coordination polyhedron of $[Ho(hfa)_3(H_2O)_2]\cdot$triglyme showing the Ho environment.

The reaction of holmium oxide with triglyme and hexafluoroacetylacetone in benzene yields air-stable adduct, $[Ho(hfa)_3(H_2O)_2]\cdot$triglyme.[8] The adduct is nonhygroscopic, can be handled in air, and is soluble in common organic solvents such as benzene, toluene, and methanol. Atmospheric pressure thermal gravimetric analysis reveals that sublimation process takes place in the 65-310 °C temperature range[9]. Over 91% of the material is vaporized leaving *ca.* 8% residue. The DTA curve shows a melting point endotherm *ca.* 70 °C which is consistent with melting point measurement (67-71 °C). 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.[10]

$$[Ln(tmhd)_3(H_2O)]+L \rightarrow [Ln(tmhd)_3L]+H_2O$$
$$(Ln=La,\ Eu,\ or\ Tb;\ L=triglyme\ or\ tetraglyme)$$

The reaction occurs with the complete elimination of the coordinated water molecules. The polyether ligand acts as a partitioning agent, removing the coordinated water due to chelate effect. However, the reaction of holmium oxide with hexafluoroacetylacetone in the presence of triglyme in benzene yields an air-stable adduct, $[Ho(hfa)_3(H_2O)_2]\cdot$triglyme which not only has water molecules coordinated to Ho atom but also holds triglyme through hydrogen bonds.

$$1/2Ho_2O_3+3Hhfa+triglyme \rightarrow [Ho(hfa)_3(H_2O)_2]\cdot triglyme$$

In $[Ho(hfa)_3(H_2O)_2]\cdot$triglyme, the triglyme ligand is not acting as a chelating ligand so that water molecules are coordinated to the holmium atom. To the best of our knowledge, this coordination mode of the polyether ligand is quite unique; such ligands are normally found either chelating and/or bridging bonding modes.[11] The coordination polyhedron of $[Ho(hfa)_3(H_2O)_2]\cdot$triglyme showing the Ho environment is shown in Figure 1. The holmium metal center is eight coordinate, with the overall coordination polyhedron being distorted square antiprismatic. The mean plane separation between two squares [O(1)-O(5)-O(6)-O(8) and O(2)-O(3)-O(4)-O(7)] is about 2.03 Å and the distance from the holmium ion to the center of the plane of the four oxygen atoms is *ca.* 1.0 Å. The angles among oxygen atoms

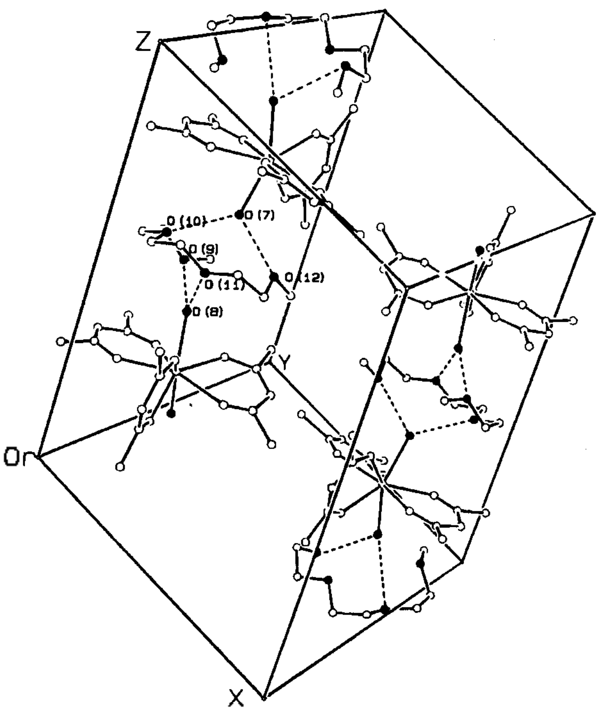

Figure 2. Unit cell packing diagram showing the chains running along the z axis.

in squares, *e.g.* O(1)-O(5)-O(6) or O(2)-O(3)-O(4), are in the range of 79.8-97.5° and the oxygen-oxygen distances in squares range from 2.71 to 2.89 Å. The Ho-O bond distances range from 2.31 to 2.36 Å. The properties of a material depend critically upon both the chemical nature of the constituent molecules and their relationships with respect to each other in the condensed phase. Thus, the preparation of new materials must be concerned with the problems of both molecular and supramolecular synthesis.[12] The most interesting feature in this molecule is that $[Ho(hfa)_3(H_2O)_2]\cdot$triglyme molecules have one-dimensional networks by intermolecular O-H···O hydrogen bonding interactions. Figure 2 shows a unit cell packing diagram consisting of two parallel rods for $[Ho(hfa)_3(H_2O)_2]\cdot$ triglyme. These hydrogen bonding interactions give chains running along the crystallographic *z* axis of the lattice. The extended rods are built up by $[Ho(hfa)_3(H_2O)_2]$ units linked with the triglyme ligands; especially between two water molecules, [O(7) and O(8)], coordinated to the holmium metal center and the oxygen atoms of the triglyme ligand. One oxygen atom of $[Ho(hfa)_3(H_2O)_2]$ unit, O(7), has an interaction via hydrogen bonds with two oxygen atoms of the triglyme ligand, [O(10), and O(12)], whereas the other oxygen atom O(8) with O(9), and O(11). (see Table 1) 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 intermolecular hydrogen bonds between the water molecules and ketonic oxygen atoms of the β-diketonate ligands present in CVD precursors have been reported to contribute significantly to the heat of vaporization[11]; water acts as a source of vapor pressure reduction. However, the unique intermolecular hydrogen bond in $[Ho(hfa)_3(H_2O)_2]\cdot$

Table 1. Selected O-O Distances [Å] and Angles [deg] for [Ho(hfa)$_3$(H$_2$O)$_2$]·triglyme

O(7)···O(9)	3.56*	O(8)···O(9)	2.71
O(7)···O(10)	2.80*	O(8)···O(10)	3.16
O(7)···O(11)	3.16*	O(8)···O(11)	2.87
O(7)···O(12)	2.77*	O(8)···O(12)	3.71
O(10)*···O(7)···O(12)*	104.6	O(9)···O(8)···O(11)	101.7

*symmetry operation: x, 0.5-y, −0.5+z.

triglyme is unprecedented; the hydrogen bonding interaction between water molecules and the oxygen atoms of the triglyme ligand results in the one-dimensional chain. It will be interesting to understand the role of the outer-sphere polyether ligand for CVD precursors during vaporization. Further studies on the role of triglyme ligand during vaporization and on the vapor phase structure are in progress in our laboratory.

Acknowledgment. Prof. J. Ko at Korea University was appreciated for generous loans of chemicals.

Supporting Information Available. Experimental details of X-ray crystal structure determination, crystallographic tables, listing of atomic coordinates, thermal parameters, and bond distances and angles (19 pages).

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6. Crystal data for [Ho(hfa)$_3$(H$_2$O)$_2$]·triglyme; monoclinic $P2_1/c$, a=12.559(3), b=19.111(6), c=16.789(6) Å, β=110.59(4)°, V=3772(2) Å^3. The structure was solved by a heavy atom method and refined to R_1=0.047 and wR_2=0.121 against 2732 observed $[I>2\sigma(I)]$ reflections.
7. Abbreviations used in this paper include: Hhfa, hexafluoroacetylacetone; hfa, anion of Hhfa; diglyme, bis(2-methoxyethyl) ether; triglyme, triethylene glycol dimethyl ether; tetraglyme, tetraethylene glycol dimethyl ether; tmhd, 2,2,6,6-tetramethylheptane-3,5-dione.
8. To a suspension of Ho$_2$O$_3$ (1.00 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 resulting mixture was refluxed for 40 h. After cooling the mixture was filtered and the resulting yellow solution was removed in vacuo to yield pale yellow powders. Slow evaporization of benzene solution gave pale yellow crystals suitable for X-ray crystallography. Yield: 52%. IR (KBr, cm^{-1}): 3400 (m), 2980 (m), 1655 (s), 1559 (m), 1530 (m), 1505 (s), 1255 (s), 1205 (s), 1149 (s), 1100 (s), 1020 (m), 800 (s), 655 (s), 590 (m).
9. Experiment was performed on a SETARAM TGA-92 instrument, which simultaneously carried out thermogravimetry (TGA) and differential thermal analysis (DTA). The measurement was 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.
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A Mechanistic Study on Nucleophilic Additions of Amines to 3-Butyn-2-one and Formation of 3-Methylpyrazole

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Received December 17, 1996

Nucleophilic additions to triple bonds have been intensively studied due to the diversity of synthetic interests.[1-4] One of the most investigated mechanism is addition mechanism of amines to activated acetylenes.[5,6] However, this mechanism has not been fully understood. Our recent study has revealed that the reactions of methyl propiolate (HC≡