

Communications

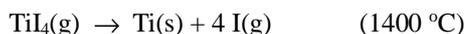
Synthesis and Characterization of an Eight-Coordinated [Ho(hfa)₂(triglyme)][Ho(hfa)₄] Holmium Complex

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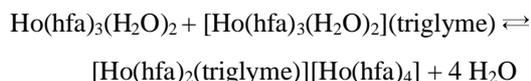
In the early 1950s, deposition by chemical reaction of gas phase precursors was mostly a laboratory curiosity with few applications. Of particular interest was the process for the refining transition metals by displacement of their precursors.¹



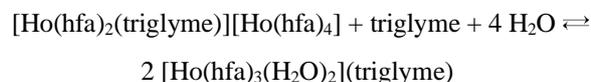
Today the technique for the deposition of thin film of metals is an indispensable tool in microelectronics processing.² Essential to the technique is volatile precursors that do not decompose during vaporization. In addition, precursors should be non-toxic and nonpyrophoric, easy to handle and pure. Metal β -diketonates meet most of these criteria, being relatively stable when vaporized, non-pyrophoric and easy to handle.³ Recently, the lanthanide β -diketonates have been extensively studied as precursors for the growth of superconducting thin film by CVD.⁴ Most of the lanthanide β -diketonates precursors are molecular species having polyether ligands.⁵⁻⁷ In this work we report the preparation and characterization of the holmium salt having high volatility; [Ho(hfa)₂(triglyme)][Ho(hfa)₄].

The holmium salt, [Ho(hfa)₂(triglyme)][Ho(hfa)₄], was quantitatively synthesized from the reaction of Ho(hfa)₃(H₂O)₂ and [Ho(hfa)₃(H₂O)₂](triglyme) in benzene.⁸ The driving force for the synthesis of [Ho(hfa)₂(triglyme)][Ho(hfa)₄] is mainly the poor solubility of the product in benzene and the replacement of four water molecules bound

to Holmium metal by one triglyme is surely favorable from the entropy point of view. Furthermore, [Ho(hfa)₂(triglyme)][Ho(hfa)₄] in 95% of ethyl alcohol at room temperature slowly decomposes by disproportionation to the Ho(hfa)₃(H₂O)₂ and [Ho(hfa)₃(H₂O)₂](triglyme). This shows that the interconversion is reversible.



The sublimation of the solid [Ho(hfa)₃(H₂O)₂] · triglyme at 80 °C also produced the [Ho(hfa)₂(triglyme)][Ho(hfa)₄] salt. We are not sure that this is only the product but major product. This [Ho(hfa)₂(triglyme)][Ho(hfa)₄] compound was reversibly interconverted to [Ho(hfa)₃(H₂O)₂](triglyme) in the presence of triglyme and water.



The molecular structure of [Ho(hfa)₂(triglyme)][Ho(hfa)₄] reveals that one of the holmium atom is exclusively coordinated to four hfa ligands in an antisquareprismatic arrangement, whilst the other is encapsulated by hfa and triglyme ligands.⁹

The structure of the [Ho(hfa)₂(triglyme)] cation consists of two hfa ligands one above and one below the planar holmium-coordinating triglyme. The two O-Ho-O planes of the hfa chelate rings intersect at an angle of 9.1°, so that the hfa oxygens are coordinated in an almost planar confi-

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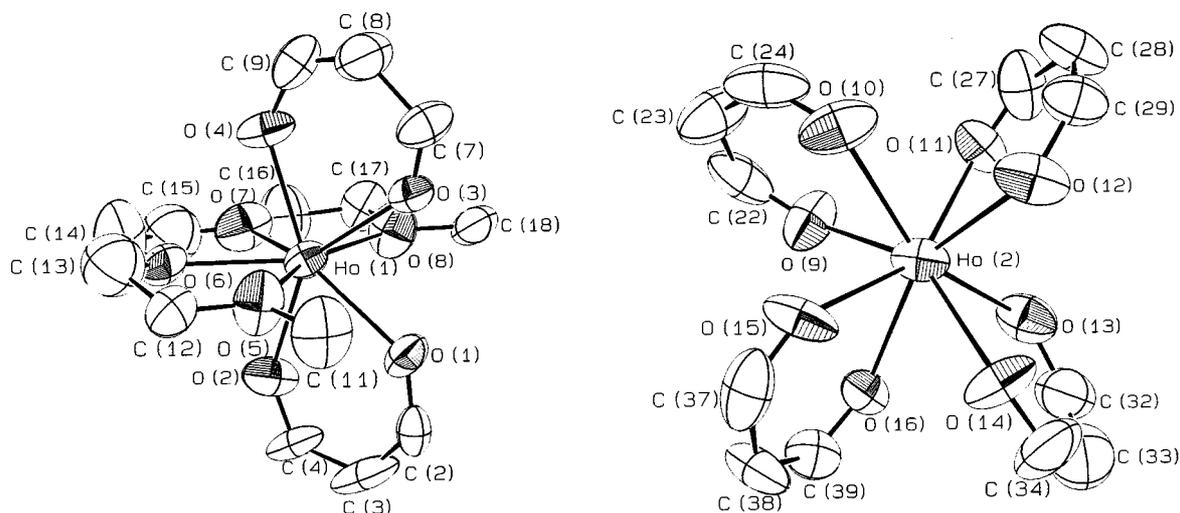


Figure 1. ORTEP diagrams of the crystal structure of $[\text{Ho}(\text{hfa})_2(\text{triglyme})][\text{Ho}(\text{hfa})_4]$ showing the atomic labelling scheme and thermal ellipsoidal at 50% level. The CF_3 groups and hydrogen atoms are omitted for clarity.

guration. The two HoO_4 planes $[\text{Ho}(1)\text{-O}(1)\text{-O}(2)\text{-O}(3)\text{-O}(4)]$ and $[\text{Ho}(1)\text{-O}(5)\text{-O}(6)\text{-O}(7)\text{-O}(8)]$ intersect at an angle of 85.2° . Triglyme ligand is a linear polyether, not cyclic. Two hfa ligands lean toward the open site of the triglyme ligand mainly due to the steric unclouing. The Ho-O(of hfa) bond distances [2.30 to 2.32 Å] are shorter than the Ho-O(of triglyme) bond distances [2.35 to 2.37 Å]. The metal center of the $[\text{Ho}(\text{hfa})_4]$ anion is surrounded by the four hfa ligands to form an almost spherical molecule. The average Ho-O(of hfa) distance of the $[\text{Ho}(\text{hfa})_4]$ anion is 2.33[2] Å and the average O-Ho-O angle of the same hfa ligand is 73.4° . The crystal structure of $\text{CsY}(\text{hfa})_4$ had been published. The average Y-O(of hfa) distance of the $[\text{Y}(\text{hfa})_4]$ anion is 2.32 Å and the average O-Y-O angle of the same hfa ligand is 73.5° .⁶ Atmospheric pressure thermal gravimetric analysis reveals that sublimation process takes place in the 150-260 °C temperature range.¹⁰ Over 99% of the material is vaporized leaving about 1% residue. In general, ionic salts show the high melting point and low volatility. However, $[\text{Ho}(\text{hfa})_2(\text{triglyme})][\text{Ho}(\text{hfa})_4]$ shows relatively low melting point and high volatility. The DTA curve shows a melting point endothermal at 180 °C which is consistent with melting point measurement (176-179 °C). In $[\text{Ho}(\text{hfa})_2(\text{triglyme})][\text{Ho}(\text{hfa})_4]$, the predominant peak observed is $[\text{Ho}(\text{hfa})_2(\text{triglyme})]$ at m/z 757.

Supporting Information Available. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-205686). 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: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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7. Abbreviations used in this paper include: Hhfa, hexafluoropentanedione; hfa, anion of Hhfa; triglyme, triethylene glycol dimethyl ether.
8. To a Schlenk flask containing $\text{Ho}(\text{hfa})_5(\text{H}_2\text{O})_2$ (0.036 g, 0.044 mmol) and $[\text{Ho}(\text{hfa})_5(\text{H}_2\text{O})_2]\text{-triglyme}$ (0.044 g, 0.044 mmol) was added 10 mL of benzene. The resulting mixture was refluxed for 0.5 h. Upon stirring the precipitates were formed. The ivory precipitates were collected on a suction frit and washed with benzene. Yield: 0.07 g, 91%. Slow evaporation of the product in 1 : 10 solution of methyl alcohol: toluene gave white-yellow crystals suitable for X-ray crystallography. mp: 172 °C. IR (KBr, cm^{-1}): 3140 (w), 2960 (w), 1650 (s), 1560 (s), 1530 (s), 1508 (s), 1480 (m), 1460 (m), 1440 (w), 1430 (w), 1260 (s), 1210 (s), 1140 (s), 1090 (m), 1080 (m), 1060 (m), 1025 (w), 1012 (w), 1000 (w), 940 (w), 880 (w), 840 (w).
9. Crystal data for $[\text{Ho}(\text{hfa})_2(\text{triglyme})][\text{Ho}(\text{hfa})_4]$; orthorhombic Fdd2, $a = 38.439(3)$, $b = 41.206(3)$, $c = 15.596(2)$ Å, $V = 24704(4)$ Å³. The structure was solved by a heavy atom method and refined to $R1 = 0.061$ and $wR2 = 0.147$ against 5018 observed [$I > 2\sigma(I)$] reflections.
10. 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.