13. (a) Whittington, B. I.; Anderson, J. R. *J. Phys. Chem.* **1993**, *97*, 1032. (b) Reddy, K. R.; Ramaswamy, A. V.; Ratnasamy, P. *J. Catal.* **1993**, *143*, 275. (c) Centi, G.; Perathoner, S.; Trifiro, F.; Aboukais, A.; Aissi, C. F.; Guelton, M. *J. Phys. Chem.* **1992**, *96*, 2617. (d) Prasada Rao, P. R. H.; Ramaswamy, A. V.; Ratnasamy, P. *J. Catal.* **1993**, *141*, 604. (e) Tuel, A.; Ben Tarrit, Y. *Appl. Catal. A.: General* **1993**, *102*, 201. (f) Hari Prasad Rao, P. R.; Ramaswamy, A. V.; Ratnasamy, P. *J. Catal.* **1992**, *137*, 225.
14. Luan, Z.; Cheng, C.-F.; Zhou, W.; Klinowski, J. *J. Phys. Chem.* **1995**, *99*, 1018.
15. (a) Barrer, R. M. In *Zeolites, Synthesis, Structure, Technology and Application*; Drzaj, B.; Hocevar, S.; Pejovnik, S., Eds.; Elsevier: New york, 1985; p 1. (b) Kessler, H. In *Recent Advances in Zeolite Science*; Klinowski, J.; Barrie, P. J., Eds.; Elsevier: New York, 1989; p 17. (c) Liu, J.; Kim, A. Y.; Virden, J. W.; Bunker, C. *Langmuir* **1995**, *11*, 689.
16. Engelhard, G.; Michel, D. *High Resolution Solid-State NMR of Silicates and Zeolites*; Wiley: New York, 1987.
17. Lapina, O. B.; Mastikhin, V. M.; Shubin, A. A.; Krasilnikov, V. N.; Zamarav, K. *Progr. NMR Spectrosc.* **1992**, *24*, 457.
18. Rigutto, M. S.; van Bekkum, H. *Appl. Catal.* **1991**, *68*, L1.
19. (a)Mastikhin, V. M.; Polyakova, G. M.; Ziolkowsky, J.; Borescov, G. K. *Kinet. Katal.* **1970**, *11*, 1463. (b) Lapina, O. B.; Mastikhin, V. M.; Nosov, A. V.; Beutel, T.; Knozinger, H. *Catal. Lett.* **1992**, *13*, 203.
20. (a) Taouk, B.; Guelton, M.; Grimblot, J.; Bonnelle, J. P. *J. Phys. Chem.* **1988**, *92*, 6700. (b) Eckert, H.; Wachs, I. E. *J. Phys. Chem.* **1989**, *93*, 6796. (c) Das, N. D.; Eckert, H.; Hu, H.; Wachs, I. E.; Walzer, J. F.; Feber, F. J. *J. Phys. Chem.* **1993**, *97*, 8240.
21. Chen, J.; Li, Q.; Xu, R.; Xiao, F. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2694.

Synthesis and Characterization of Volatile and Thermally Stable Europium β-Diketonate Complexes

Seong-Joo Kang*, Young Sook Jung, and Youn Soo Sohn†

Department of Chemical Education, Korea National University of Education, 363-791 Cheongwon, Chungbuk, Korea
†Inorganic Chemistry Laboratory, Korea Institute of Science and Technology, Seoul 136-791, Korea
Received October 7, 1996

Preparation and properties of $Eu(hfa)_3 \cdot L$ (Hhfa=hexafluoroacetylacetone, L=bis(2-methoxyethyl)ether, diglyme, and 2,2':6',2"-terpyridine, tpy), which are potential CVD precursors for europium, were investigated. The reaction of the Eu_2O_3 with Hhfa in the presence of tridentate neutral ligand yielded the nine-coordinated $Eu(hfa)_3 \cdot L$. $Eu(hfa)_3 \cdot$diglyme is air- and moisture-stable and most importantly has good volatility and thermal stability. $Eu(hfa)_3 \cdot$tpy shows no sublime intact. The complex $Eu(hfa)_3 \cdot$diglyme has been characterized by an X-ray structure determination; monoclinic $P2_1/n$, a=10.252(1), b=16.051(6), c=19.392(8) Å, β=96.10(2)°, V= 3173(2) Å^3. The europium atom in $Eu(hfa)_3 \cdot$diglyme adopts a square-antiprismatic geometry with the ninth coordinating oxygen atom capping one of the square faces. All the adducts have been characterized by IR, TGA/DTA.

Introduction

There has been considerable interest in recent years in the development of new precursors for the chemical vapor deposition (CVD) of inorganic materials.[1] In general, such precursors must be volatile, stable to transport to the deposition site, and decompose cleanly to give the desired material. MOCVD allows for the exact control of the film microstructure and stoichiometry which is essential for the manufacture of superconducting devices with optimal and reproducible properties. The chemistry of rare-earth metal β-diketonates and alkoxides is in the progress of rapid development in the last 5 years. The major foreseeable application of such precursors is in the synthesis of electroceramics, *e.g.* superconductors such as $Pb_2Sr_2LnCu_3O_{8-x}$,[2] $LnBa_2Cu_3O_{7-x}$,[3] and $La_{2-x}Sr_xCuO_4$,[4] piezoelectrics such as $LaCuO_2$,[5] as phosphors,[6] and NMR shift reagents,[7] *e.g.* $[\{Eu(tmhd)_3\}_2]$, and $[\{Pr(tmhd)_3\}_2]$,(Htmhd=2,2,6,6-tetramethylheptane-3,5-dione). The coordination and the properties of the rare-earth metal compounds[8] can be conveniently modulated by a proper choice of the coordinated ligands (and of the oxidation number of the central metal) in order to obtain suitable volatility and stability to oxygen and moisture and a convenient pyrolytic decomposition mode to give the desired product. In this paper, preparation and properties of $Eu(hfa)_3 \cdot L$ (L=diglyme or tpy) are described. Volatility and stability of two compounds have been compared and the results are expected to envisage for the better CVD precursors of inorganic materials.

Experimental Section

General procedures. All manipulations were performed under an inert atmosphere using Schlenk techniques. All solvents were distilled by standard techniques. Europium oxide, Hhfa, and diglyme were purchased from Aldrich and used as received. 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 Eu(hfa)$_3$·diglyme, 1. To a suspension of Eu_2O_3 (1.23 g, 3.5 mmol) in benzene (170 mL) were added Hhfa (2.97 mL, 21 mmol) and diglyme (1.00 mL, 7 mmol). The resulting mixture was refluxed for 15 h. On cooling to room temperature the remaining europium oxide was filtered off and the resulting yellow solution was removed in vacuo to yield white crystalline powders. The solid was then washed with hexane and dried under vacuum. Slow evaporation of benzene solution gave pale yellow crystals suitable for X-ray crystallography. Yield: 4.70 g, 75%. The melting point of the product was 75-78 °C. IR (KBr, cm^{-1}): 1652 (s), 1602 (m), 1559 (m), 1531 (m), 1496 (s), 1259 (s), 1213 (s), 1149 (s), 1078 (w), 1045 (w), 1010 (w), 981 (w), 872 (w), 800 (m), 745 (m), 661 (m), 585 (m).

Preparation of Eu(hfa)$_3$·tpy, 2. To a suspension of Eu_2O_3 (1.23 g, 3.5 mmol) and tpy (1.63 g, 7.0 mmol) in benzene (170 mL) were added Hhfa (2.97 mL, 21 mmol). The resulting mixture was refluxed for 2 d. On cooling to room temperature the excess of europium oxide was filtered off and the resulting yellow-pink solution was removed in vacuo to yield pale pink crystalline powders. The solid was then washed with methanol and dried under vacuum. Slow evaporation of hexane solution gave pale pink crystalline needles. Yield: 4.93 g, 70%. The melting point of the product was 235-240 °C. IR (KBr, cm^{-1}): 1670 (s), 1652 (s), 1602 (m), 1580 (w), 1559 (m), 1531 (m), 1496 (s), 1450 (w), 1380 (w), 1257 (s), 1213 (s), 1149 (s), 1100 (w), 1010 (w), 800 (m), 870 (s), 661 (m), 585 (m).

X-ray Crystal Analysis. The crystal of Eu(hfa)$_3$·diglyme was mounted onto a glass fiber with epoxy cement. The X-ray data were collected on an Enraf-Nonius CAD4 automatic diffractometer with graphite-monochromated Mo Kα (λ=0.71073 Å) at ambient temperature. Unit cell dimensions were based on 25-well centered reflections by using a least-square procedure. Three standard reflections monitored every hour showed no significant intensity variation over the data collection. The total of 4058 intensities measured within a θ range 2.0-24.9°, yielded 3832 unique and 2500 observed [Fo>3σ(F)] reflections (merging R= 0.020). The data were corrected for Lorentz and polarization effects. Absorption effects were corrected for by the empirical φ-scan method.[9] The structure were solved by the Patterson method (SHELXS-86) and were refined by full-matrix least squares techniques (SHELXL-93) to give a final R-value of 0.045 for 3776 observed data and 442 parameters. 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.[10] Crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1. The fractional coordinates is given in Table 2 and selected bond lengths and angles in Table 3.

Table 1. Crystal Data and Structure Refinement for Eu(hfa)$_3$·diglyme

formula	$C_{21}H_{17}EuF_{18}O_9$
fw	907.31
T (°C)	20
wavelength, Å	0.71073
space group	$P2_1/n$ (No. 14)
a, Å	10.252(1)
b, Å	16.051(6)
c, Å	19.392(8)
β, deg	96.10(2)
V, Å^3	3173(2)
Z	4
ρ_{calcd}, gcm^{-3}	1.899
μ(Mo Kα), cm^{-1}	21.27
no. of rflns collctd	4058
no. of indep rflns	3832 [R(int)=0.0186]
no. of params	442
GOF on F^2	1.115
final R indices [I>2σ(I)]	R1[a]=0.0449, wR2=0.1245
R indices (all data)	
largest diff. peak and hole, e Å^{-3}	R1=0.0460, wR2=0.1257

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

Results and Discussion

Synthesis. The strategy for the synthesis of the anhydrous CVD precursors has been extensively studied, since the potential CVD precursors containing coordinated water have poor mass transport properties and volatility.[11] The molecular architecture for the CVD precursor can be modified by adding a "multipronged" Lewis base, such as glyme, thereby plugging into possible vacant coordination sites. The single-step reaction of europium oxide with hexafluoroacetylacetone and tridentate neutral ligand in benzene has been found to yield reproducible monomeric air stable adducts.

$$Eu_2O_3 + 6Hhfa + 2diglyme \rightarrow 2Eu(hfa)_3\cdot diglyme + 3H_2O$$

This procedure yields anhydrous potential europium CVD precursor even water is the by-product. The hard Lewis base, diglyme, encapsulates the europium metal ion thus competing with H_2O molecules in saturating the coordination sphere. The present procedure also yields non-hygroscopic adducts through a low cost route. This represents

an important aspect for materials used for CVD applications where low-cost chemicals that may be manipulated on open benches are an important objective.

X-ray Structure Determination. The molecular structure of $Eu(hfa)_3 \cdot$ diglyme is shown in Figure 1, with the CF_3 groups of hfa and terminal CH_3 groups of diglyme omitted for clarity. The europium atom binds to all three bidentate hfa ligands and to three oxygen atoms of the diglyme ligand thus resulting in an europium coordination of nine.

A square-antiprismatic geometry is obtained with the ninth coordinating oxygen atom [O(7)] capping one of the square faces (see Figure 2).

The mean plane separation between two squares is about 2.43 Å and two squares are nearly parallel (the angle between two squares is 1.96°). The angles among oxygen atoms in square, *e.g.* O(1)-O(5)-O(3) or O(2)-O(6)-O(4), are in the range of 85.7-95.8°. The two hfa oxygens of each ligand are attached to the opposite top and bottom vertices of the prism. Selected bond distances and angles are listed in Table 3. In this molecule the Eu-O bond distances fall into two distinctly different groups; those to the β-diketonate ligands and those for the diglyme ligand.

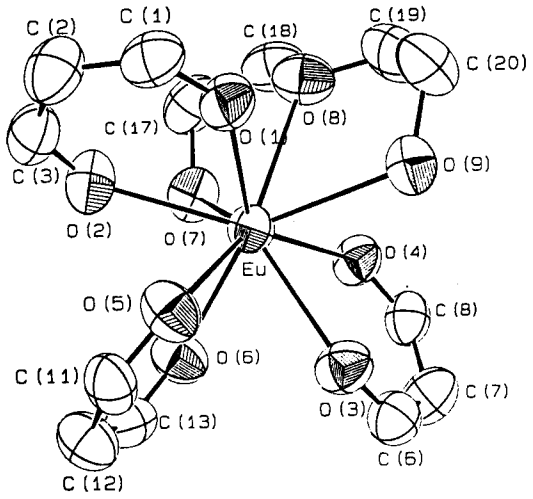

Figure 1. ORTEP drawing of the crystal structure of $Eu(hfa)_3 \cdot$ diglyme showing the atomic labeling scheme and thermal ellipsoidal at the 50% level. CF_3 groups of the hfa and terminal CH_3 groups of diglyme have been omitted for clarity.

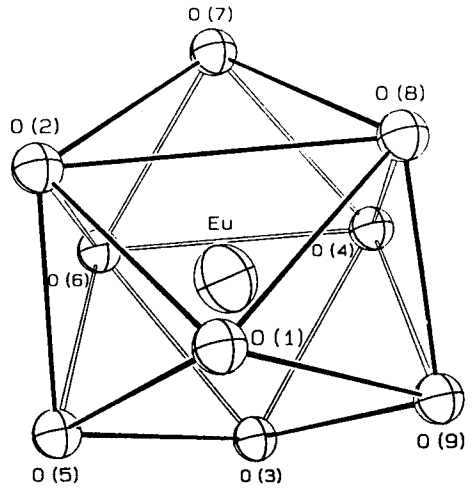

Figure 2. Co-ordination polyhedron of $Eu(hfa)_3 \cdot$ diglyme showing the Eu environment.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $Eu(hfa)_3 \cdot$ diglyme

	x	y	z	U(eq)[a]
Eu	2422(1)	1044(1)	2378(1)	50(1)
O(1)	866(5)	1745(4)	3023(3)	60(1)
O(2)	2260(7)	313(4)	3455(3)	69(2)
O(3)	3982(6)	1953(4)	1893(3)	64(2)
O(4)	2558(6)	680(4)	1187(3)	61(1)
O(5)	3667(5)	1805(4)	3299(3)	62(2)
O(6)	4491(6)	399(4)	2570(3)	65(2)
O(7)	2124(6)	−518(4)	2217(3)	68(2)
O(8)	138(6)	605(4)	1857(3)	71(2)
O(9)	1113(6)	2142(4)	1627(3)	68(2)
F(1)	−1087(8)	2170(5)	4296(5)	137(3)
F(2)	−1190(14)	2581(10)	3287(6)	246(9)
F(3)	197(13)	3018(6)	3990(8)	211(7)
F(4)	3482(11)	−185(9)	4690(6)	207(6)
F(5)	1823(14)	51(8)	5165(4)	210(6)
F(6)	1868(15)	−855(7)	4474(7)	202(6)
F(7)	6508(11)	2438(11)	1918(6)	246(9)
F(8)	5379(11)	3271(7)	1437(9)	220(7)
F(9)	6389(10)	2483(7)	883(6)	194(5)
F(10)	3427(14)	696(8)	−461(4)	211(6)
F(11)	1656(11)	450(9)	−127(5)	195(5)
F(12)	3100(13)	−341(6)	95(4)	169(5)
F(13)	6038(9)	2086(5)	4662(4)	148(4)
F(14)	4128(12)	2341(13)	4594(8)	302(12)
F(15)	5214(21)	2977(6)	4084(7)	295(12)
F(16)	−2284(7)	141(7)	3170(6)	175(5)
F(17)	−3264(12)	−177(12)	2256(7)	245(9)
F(18)	−3580(12)	−784(7)	3070(12)	267(10)
C(1)	564(9)	1700(6)	3612(5)	64(2)
C(2)	942(11)	1134(7)	4123(5)	74(3)
C(3)	1785(10)	481(6)	4009(5)	69(2)
C(4)	−434(14)	2347(8)	3792(7)	92(3)
C(5)	2237(17)	−89(10)	4598(6)	106(4)
C(6)	4568(8)	1931(6)	1371(5)	63(2)
C(7)	4273(11)	1467(6)	779(5)	75(3)
C(8)	3259(9)	886(5)	735(5)	61(2)
C(9)	5700(12)	2529(9)	1380(7)	91(4)
C(10)	2910(13)	444(8)	54(5)	84(3)
C(11)	4740(9)	1679(6)	3638(4)	62(2)
C(12)	5681(9)	1078(6)	3531(5)	70(2)
C(13)	5498(9)	514(6)	2990(5)	67(2)
C(14)	5056(13)	2251(8)	4251(6)	89(3)
C(15)	−3385(12)	−75(10)	2887(8)	98(4)
C(16)	2795(13)	−1016(7)	1749(6)	91(3)
C(17)	762(11)	−741(7)	2234(6)	84(3)
C(18)	−65(10)	−266(7)	1717(6)	81(3)
C(19)	−496(11)	1105(8)	1317(6)	94(4)
C(20)	−279(10)	1999(8)	1517(6)	89(3)
C(21)	1412(14)	2978(8)	1595(8)	121(5)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for Eu(hfa)$_3$·diglyme

Eu-O(1)	2.408(5)	Eu-O(2)	2.416(6)
Eu-O(3)	2.427(6)	Eu-O(4)	2.401(6)
Eu-O(5)	2.414(5)	Eu-O(6)	2.354(6)
Eu-O(7)	2.540(6)	Eu-O(8)	2.548(6)
Eu-O(9)	2.571(6)	O(1)-C(1)	1.216(10)
O(2)-C(3)	1.256(10)	O(3)-C(6)	1.231(10)
O(4)-C(8)	1.236(10)	O(5)-C(11)	1.237(10)
O(6)-C(13)	1.259(11)	O(7)-C(16)	1.439(12)
O(7)-C(17)	1.445(12)	O(8)-C(18)	1.435(12)
O(8)-C(19)	1.421(13)	O(9)-C(21)	1.379(13)
C(1)-C(2)	1.369(14)	C(1)-C(4)	1.52(2)
C(2)-C(3)	1.390(14)	C(3)-C(5)	1.50(2)
C(6)-C(7)	1.375(13)	C(6)-C(9)	1.505(14)
C(7)-C(8)	1.392(13)	C(8)-C(10)	1.509(14)
C(11)-C(12)	1.395(13)	C(11)-C(14)	1.511(13)
C(12)-C(13)	1.383(13)	C(13)-C(15)	1.514(14)
C(17)-C(18)	1.46(2)	C(19)-C(20)	1.50(2)
O(1)-Eu-O(2)	70.6(2)	O(1)-Eu-O(3)	114.9(2)
O(1)-Eu-O(4)	136.3(2)	O(1)-Eu-O(5)	72.9(2)
O(1)-Eu-O(6)	139.4(2)	O(1)-Eu-O(7)	116.6(2)
O(1)-Eu-O(8)	72.8(2)	O(1)-Eu-O(9)	68.8(2)
O(2)-Eu-O(3)	137.3(2)	O(2)-Eu-O(4)	136.9(2)
O(2)-Eu-O(5)	71.7(2)	O(2)-Eu-O(6)	78.1(2)
O(2)-Eu-O(7)	67.0(2)	O(2)-Eu-O(8)	93.7(2)
O(2)-Eu-O(9)	137.9(2)	O(3)-Eu-O(4)	70.5(2)
O(3)-Eu-O(5)	70.3(2)	O(3)-Eu-O(6)	72.9(2)
O(3)-Eu-O(7)	128.4(2)	O(3)-Eu-O(8)	128.9(2)
O(3)-Eu-O(9)	72.2(2)	O(4)-Eu-O(5)	139.0(2)
O(4)-Eu-O(6)	84.4(2)	O(4)-Eu-O(7)	70.1(2)
O(4)-Eu-O(8)	72.3(2)	O(4)-Eu-O(9)	72.7(2)
O(5)-Eu-O(6)	73.1(2)	O(5)-Eu-O(7)	129.6(2)
O(5)-Eu-O(8)	145.5(2)	O(5)-Eu-O(9)	105.9(2)
O(6)-Eu-O(7)	71.4(2)	O(6)-Eu-O(8)	135.7(2)
O(6)-Eu-O(9)	142.9(2)	O(7)-Eu-O(8)	65.5(2)
O(7)-Eu-O(9)	123.9(2)	O(8)-Eu-O(9)	64.1(2)
C(1)-O(1)-Eu	135.1(6)	C(3)-O(2)-Eu	134.8(6)
C(6)-O(3)-Eu	134.5(6)	C(8)-O(4)-Eu	135.6(6)
C(11)-O(5)-Eu	132.9(6)	C(13)-O(6)-Eu	134.5(6)
C(16)-O(7)-Eu	124.5(6)	C(17)-O(7)-Eu	110.2(6)
C(18)-O(8)-Eu	116.9(6)	C(19)-O(8)-Eu	117.7(6)
C(20)-O(9)-Eu	115.2(6)	C(21)-O(9)-Eu	126.0(7)
C(16)-O(7)-C(17)	113.9(8)	C(18)-O(8)-C(19)	111.4(8)
C(20)-O(9)-C(21)	111.6(9)	O(1)-C(1)-C(2)	129.6(9)
O(1)-C(1)-C(4)	114.8(9)	O(2)-C(3)-C(2)	127.0(9)
O(2)-C(3)-C(5)	113.9(10)	O(3)-C(6)-C(7)	128.2(9)
O(3)-C(6)-C(9)	114.6(9)	O(4)-C(8)-C(7)	128.5(8)
O(4)-C(8)-C(10)	113.1(9)	O(5)-C(11)-C(12)	128.7(8)
O(5)-C(11)-C(14)	115.0(9)	O(6)-C(13)-C(12)	128.5(9)
O(7)-C(17)-C(18)	110.4(8)	O(8)-C(18)-C(17)	108.5(8)
O(8)-C(19)-C(20)	107.9(8)	O(9)-C(20)-C(19)	107.9(9)
C(1)-C(2)-C(3)	121.2(8)	C(2)-C(1)-C(4)	115.5(9)
C(2)-C(3)-C(5)	119.2(9)	C(6)-C(7)-C(8)	120.7(9)
C(7)-C(6)-C(9)	117.1(9)	C(7)-C(8)-C(10)	118.4(9)
C(12)-C(11)-C(14)	116.3(8)	C(13)-C(12)-C(11)	121.6(8)

The Eu-O(of hfa) bond distances [2.354(6) to 2.427(6) Å] are, as expected, much shorter than the Eu-O(of glyme) bond distances [2.540(6)-2.571(6) Å]. This is indicative of weak coordinative bonds between the metal center and the oxygen atoms of the diglyme ligand.

Table 4. The Average Lengths of Eu-O(of β-diketonate), Coordination Number and Geometry for the Eu(β-diketonate) Complexes

Comp.	Average lengths of Eu-O(of β-diketonate)	Coordination number	Geometry
Eu(tmhd)$_3$·triglyme	2.33[1] Å	8	sq. an.*
Eu(tmhd)$_3$·(py)$_2$	2.35[1] Å	8	sq. an.
Eu(tmhd)$_3$·(DMF)$_2$	2.36[1] Å	8	sq. an.
Eu(hfa)$_3$·diglyme	2.40[1] Å	9	cap. sq. an.

*sq. an.; square antiprism. cap. sq. an.; capped square antiprism

The tendency of Eu-O bond distances is comparable with the La-O distances of the lanthanium analogue. In the lanthanium analogue[10] the La-O(of hfa) bond distances [2.462(6)-2.635(6) Å] are quite close to the La-O(of diglyme) bond distances [2.475(5)-2.642(6) Å]. In the Ln-O (of hfa) bond distances (Ln=Eu or La) the average Eu-O (of hfa) bond distance is approximately 0.1 Å shorter than the corresponding La-O distance. These differences are almost certainly in part due to the significantly different ionic radii of the metal centers involved [La^{3+} (1.06)>Eu^{3+} (0.85 Å)]. In the europium β-diketonate complexes, the coordination number of nine for the Eu(hfa)$_3$·diglyme is uncommon. This nine coordination might increase the steric repulsion among the coordinated atoms so that the average bond length of the Eu-O(of hfa) for the Eu(hfa)$_3$·diglyme [2.40(1) Å] is longer than that for the other eight coordinated europium complexes[13] [2.22(1)-2.36(1) Å] (Table 4).

This indicates that the size of the central metal, ligand and coordination number affect the bond strength of the metal-coordinated atom and also the volatility of the lanthanium precursors. Eu(hfa)$_3$·diglyme has no intermolecular interaction which is a good indication for the CVD precursor.[14] A further important observation is their excellent stability to both air and moisture. There is retention of essentially gauche geometry about the C-C bonds within the diglyme ligand.

TGA/DTA. TGA measurements have found extensive application where a study of weight loss versus temperature can give important insight into the breakdown and thermal behaviour of materials at elevated temperature. DTA measurements allow to study the enthalpy change occurring during the thermolysis and to know whether a reaction is occurring.

The TGA curve of Eu(hfa)$_3$·diglyme is reported in Figure 3. The TGA plot shows a singular sublimation step in the 150-295 °C temperature range. This indicates that Eu(hfa)$_3$·diglyme is a stable precusor which delivers the homoleptic diglyme complex into the gas phase easily. The absence of the intermolecular interactions explains why this compound sublimes easily without decomposition. No carbonaceous residues have been found in this case. The DTA curve of Eu(hfa)$_3$·diglyme shows a melting point endotherm at 73 °C and two other changes, the first at 80 °C and the second at 300 °C.[15] The first endothermic peak at 80 °C is presumably

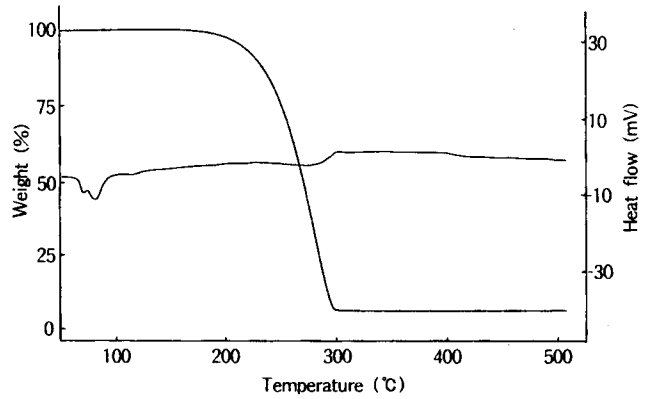

Figure 3. TGA/DTA diagram of $Eu(hfa)_3 \cdot$ diglyme.

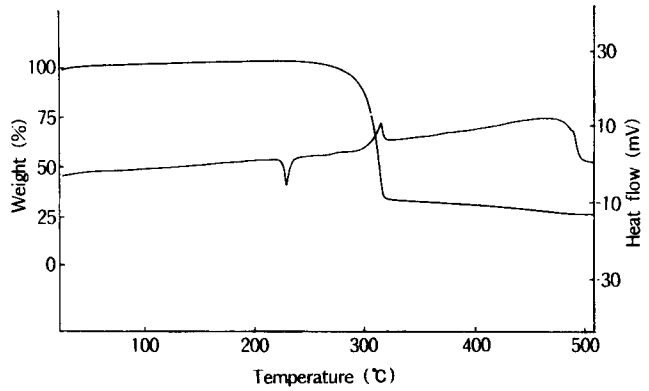

Figure 4. TGA/DTA diagram of $Eu(hfa)_3 \cdot$ tpy.

attributed to a structural phase transition. The occurrence of coordinated H_2O loss at 80 °C can be ruled out for several reasons: (i) no H_2O molecules in the crystal structure, (ii) no weight loss in the TGA plot, (iii) no IR bands in the 3300-3600 cm^{-1} range (O-H stretching). The second isotherm at 300 °C is due to the end point of sublimation. The TGA data for $Eu(hfa)_3 \cdot$ tpy reveal that this compound does not sublime intact.

Residual portion at the end of 500 °C is slightly higher than the theoretical one of Eu_2O_3(theo.; 17.4, exp.; 21.0%) The DTA data of $Eu(hfa)_3 \cdot$ tpy show a melting point endotherm at 230 °C and the other change at 315 °C for the end point of the decomposition (Figure 4).

Spectroscopic Data. The IR spectrum of complex 1 shows characteristic bands for the β-diketonates, with strong absorption bands for carbonyl group; CO stretch + CH bend at 1565-1530; C=O stretch at 1602 cm^{-1}. The bands assigned as ν(C-O-C) for diglyme occur at slightly lower frequencies than the same peak for the free ligand, 1350-1360, 1270, 1220 and also at 1110±20 cm^{-1}. The shifts from the free ligand are indicative of coordinated diglyme ligands with relatively weak Eu-O interactions. The C-F stretching frequencies of hfa group fall in the same regions as those of the C-O (diglyme). 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 Eu^{3+}.

Conclusions

The reaction of europium oxide with hexafluoroacetylacetone and tridentate neutral ligand in benzene yielded anhydrous, monomeric $Eu(hfa)_3 \cdot L$ complexes. The products have been shown to be air- and moisture-stable with good solubility in organic solvents. The X-ray structural characterization of compound 1 shows that europium metal ion is saturated with nine coordinates. The coordinative saturation of the europium ion by the multidentate Lewis base chelates and β-diketonates leads to air and moisture stable complex. TGA/DTA measurements show that $Eu(hfa)_3 \cdot$ diglyme has good mass transport properties in terms of volatility and thermal stability. $Eu(hfa)_3 \cdot$ tpy does not sublime intact even though it is air- and moisture-stable. This observation envisages the choice of the ligand; low melting point, no intermolecular interaction, coordinative saturation of the metal center.

Acknowledgment. This work was supported by Korea National University of Education Research Grant. Dr. C.-J. Kim at Korea Atomic Energy Research Institute was appreciated for the TGA/DTA discussion.

Supporting Information Available. Tables giving details of X-ray data collection parameters, atomic coordinates, anisotropic thermal parameters, bond lengths and angles, hydrogen atom parameters (6 pages); table of observed and calculated structure factors (9 pages) are available.

References

1. Lin, W.; Wiegland, B. C.; Nuzzo, R. G.; Girolami, G. S. *J. Am. Chem. Soc.* **1996**, *118*, 5977 and references there in.
2. Cava, R. J.; Ballog, B.; Krajewski, J. J.; Rupp, L. W.; Schneemeyer, L. F.; Siegrist, T.; Van Dover, R. B.; Marsh, P.; Gallagher, P. K.; Glarum, S. H.; Marshall, J. M.; Farrow, R. C.; Waszczak, J. V.; Hall, R.; Trevor, P. *Nature(London)* **1988**, *336*, 211.
3. (a) Edwards, P. P.; Harrison, M. R.; Jones, R. *Chem. Br.* **1987**, *23*, 962. (b) O'Keefe, M.; Hansen, S. *J. Am. Chem. Soc.* **1988**, *110*, 1506.
4. Bednorz, J. G.; Muller, K. A. Z. *Phys. B, Condensed Matter* **1986**, *64*, 189.
5. Muller-Buschbaum, H. *Angew. Chem.* **1989**, *28*, 1472.
6. Blasse, G. *Handbook on the Physics and Chemistry of Rare Earths*; eds. Gschneider, K. A. and Eyring, LeRoy, North Holland, Amsterdam, 1978; vol. 4, p 237.
7. Briggs, J. *J. Chem. Soc., Chem. Commun.* **1970**, 749.
8. Mehrotra, R. C.; Singh, A.; Tripathi, U. M. *Chem. Rev.* **1991**, *91*, 1287.
9. North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *24*, 351.
10. (a) Sheldrick, G. M. SHELXS-86; A Program for Structure Determination; University of Gottingen, Germany, 1986. (b) Sheldrick, G. M. SHELXL-93; A Program for Structure Refinement; University of Gottingen, Germany, 1993.
11. (a) Schulz, D. L.; Hinds, B. J.; Stern, C. L.; Marks, T. J. *Inorg. Chem.* **1993**, *32*, 249. (b) Rees, W. S.;

Caballero, C. R.; Hesse, W. *Angew. Chem. Int. Ed. Engl.* **1991**, *32*, 735. (c) Drake, S. R.; Miller, S. A. S.; Hursthouse, M. B.; Malik, K. M. A. *Polyhedron* **1993**, *12*, 1621.
12. Malandrino, G.; Licata, R.; Castelli, F.; Fragala, I. L.; Benelli, C. *Inorg. Chem.* **1995**, *34*, 6233.
13. (a) Drake, S. R.; Lyons, A.; Otway, D. J.; Slawin, A. M.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1993**, 2379. (b) Cramer, R. E.; Seff, K. *J. Chem. Soc., Chem. Commun.* **1972**, 400. (c) Cunningham, J. A.; Sievers, R. E. *Inorg. Chem.* **1980**, *19*, 595.
14. (a) Luten, H. A.; Rees Jr, W. S.; Goedken, V. L. *Chem. Vap. Deposition* **1996**, *2*, 149. (b) Schulz, D. L.; Marks, T. J. *Adv. Mater.* **1994**, *6*, 719. (c) Gleizes, A.; Sans-Lenain, S.; Medus, D.; Hovnanian, N.; Miele, P.; Foulon, J.-D. *Inorg. Chim. Acta* **1993**, *209*, 47.
15. Malandrino, G.; Castelli, F.; Fragala, I. L. *Inorg. Chim Acta*, **1994**, *224*, 203.

Molecular Engineering. Container Hosts Having Eight Undecyl Substituents Have High Solubility in Chlorinated Solvents

Kyungsoo Paek*, Kyungmi Joo, Seokjoon Kwon, Hyejae Ihm, and Yongzu Kim†

Department of Chemistry, Soong-Sil University, Seoul 156-743, Korea
Center for Biofunctional Molecules, Pohang P.O. Box 125, Pohang 790-600, Korea
†Biotech Research Institute, LG Chemical Ltd., Yu-Sung P.O. Box 61, Taejon 305-380, Korea
Received October 8, 1996

Nine new solubility-increased container hosts having eight undecyl substituents were synthesized and characterized. ^{1}H NMR spectral data showed integral inclusion state of carceplexes and their stability. ^{1}H NMR chemical shifts of guest DMA were correlated to the host's cavity dimensions shrinked by constrictive binding. Carceplex and hemicarcerand showed their distinctive FD mass spectra.

Introduction

Container hosts, carcerand and hemicarcerand, are constructed on cavitands derived from octols which are obtained by cyclotetramerization of resorcinol and aldehydes.[1] Carcerands are hosts having spherical cavity for the inclusion of guest molecules, but once the guest is captured inside it cannot escape the cavity even at high temperature unless some chemical bonds of host shell are broken.[2] Usually the guests are captured during the formation of carcerands so it exists as carceplex from the beginning. Hemicarcerands are similar to carcerands except that the guests can enter or exit the hosts interior through the shell's portals.[3] The binding energy of hemicarcerands is called a constrictive binding energy which is defined as the steric repulsions that must be overcome for dissociation of a hemicarceplex. The steric constraints are imposed by the size and shape of the guest, and those of the portal and attractions of the inner phase. Many interesting properties of hemicarcerands are reported such as shell's role as chemical reactor,[4] control of guest's in-and-out kinetics,[5] molecular container,[6] etc., which implies the tremendous applicabilities of container hosts in various fields from material sciences to medicinal chemistry.

The physicochemical properties of hemicarcerands have been controlled by variation of portal size using different functionality, number, or length of bridging units between two polar caps (hemispheres), which varies the circumstance of its core sphere.

Also the solubility of container host has been controlled mainly by using various substituents (legs) such as methyl,[2a] pentyl,[2b] or 2-phenylethyl.[2c] But still the solubility is not enough for the easy manipulation of intermediates or hosts. By incorporating dodecanal in octol, highly soluble cavitand intermediates and nine new container hosts were synthesized and characterized.

Results and Discussion

Synthesis of Highly Soluble Intermediates. Octol **1** was obtained in 83% yield from the acidic cyclotetramerization of resorcinol and dodecanal. Octol **1** itself was used as a host which binds multihydroxy guests using hydrogen bonding as well as CH-π interaction.[7] It was easily brominated to compound **2** in 87% yield with NBS in MEK at room temperature. Adjacent hydroxyl groups of compound **2** were linked using CH_2BrCl to give a rigidified tetrabromide **3** in 59% yield. Tetrabromide **3** was transformed to tetrol **4** and triol **5** using normal reaction conditions[2c] in 51% and 16% yield, respectively. The semifinal intermediates, tetrol **4** and triol **5**, were easily separated in large scale by column chromatography due to their high solubility in chlorinated solvents. Their analogues having pentyl or 2-phenylethyl substituents were much less soluble and accordingly difficult to purify, especially in large quantity.

Synthsis of Container Hosts Having Four Portals. Container hosts **6**, **7**, and **8** having four portals and un-