Effect of Polyether Ligands on Stabilities and Mass Transport Properties of a Series of Gadolinium(III) β-Diketonate Complexes

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The reaction of [Gd(tmhd)$_3$]$_2$ (**1**) (tmhd-H = 2,2,6,6-tetramethylheptane-3,5-dione) with a selected range of chelating O-donors such as, mono- {CH$_3$OCH$_2$CH$_2$OCH$_3$}, di- {CH$_3$(OCH$_2$CH$_2$)$_2$OCH$_3$}, tri- {CH$_3$(OCH$_2$CH$_2$)$_3$OCH$_3$}, tetra- {CH$_3$(OCH$_2$CH$_2$)$_4$OCH$_3$}, and heptaglyme {CH$_3$(OCH$_2$CH$_2$)$_7$OCH$_3$} in *n*-hexane at room temperature yielded the compounds [Gd(tmhd)$_3$(monoglyme)] (**2**), [Gd(tmhd)$_3$(diglyme)] (**3**), [{Gd(tmhd)$_3$}$_2$(triglyme)] (**4**), [{Gd(tmhd)$_3$}$_2$(tetraglyme)] (**5**), and [{Gd(tmhd)$_3$}$_2$(heptaglyme)] (**6**), respectively. The complexes are either monomers (**2, 3**) or dimers (**1, 4–6**) and have been characterized by microanalyses, solution cryoscopy in benzene, FT IR, mass spectrometry, and sublimation, TGA, and DSC studies. Complexes **1, 2, 5,** and **6** have also been characterized by X-ray crystallography. **1** and **6** both crystallize in the monoclinic space group P2$_1$/n, with *a* = 12.228(2) Å, *b* = 27.615(2) Å, *c* = 21.843(11) Å, and β = 105.27(6)° (**1**) and *a* = 11.773(2) Å, *b* = 18.712(3) Å, c = 21.610(3) Å, and β = 103.53(1)° (**6**). **2** and **5** crystallize in the triclinic space group P1̄ with *a* = 10.814(2) Å, *b* = 12.141(3) Å, *c* = 16.534(2) Å, α = 83.90(1)°, β = 88.20(1)°, and γ = 71.85(1)° (**2**) and *a* = 11.934(2) Å, *b* = 19.478(4) Å, *c* = 20.508(10) Å, α = 99.25(1)°, β = 106.94(2)°, and γ = 104.76(1)°, (**5**). The gadolinium ion shows a seven-coordinate distorted monocapped trigonal prismatic geometry in **1** and an eight coordinate square antiprismatic geometry in the other compounds. In **2** the monoglyme acts as bidentate chelating ligand. The tetraglyme and heptaglyme molecules in complexes **5** and **6**, respectively, act as chelating as well as bridging ligands, utilizing four of their available oxygen atoms for coordination. All these compounds are air and water stable, and those with the longer glymes have good volatilities and thermal stabilities, as demonstrated by sublimation, TGA, and DSC studies.

The clean utilization of fossil fuels is an important current problem, and fuel cells are likely to play an increasing role in the generation of electricity due to their relatively high efficiencies. Of the fuel cell systems under development, the high-temperature solid oxide fuel cell (SOFC) is the most versatile because it can operate with a variety of fuels such as natural gas (internal steam re-forming) or methanol (electrochemical oxidation).

At present, SOFC units operate around 950 °C and it is desirable to lower this to an intermediate temperature (ca. 400–600 °C) at which oxidation of methane[2] would still proceed at a satisfactory rate. Oxygen ion fluxes through mixed conducting oxides have been surveyed by Steele,[3] and materials are available[4] that can satisfy the SOFC's requirements at 400–600 °C. The electrolyte composition Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ satisfies these conditions at 500 °C.

The traditional ceramic preparation of metal oxides is from the metal hydroxide or carbonate and generally requires high-temperature processing at ca. 1000 °C in order to achieve intimate mixing of reactants.[5] High-temperature processing is undesirable for several reasons, including high energy cost, an

inability to gain access to metastable phases only at lower temperatures, and stress buildup in films. An alternative strategy uses metal alkoxides [M(OR)$_n$],[6] where the metal is bound only to oxygen atoms. Their synthesis by low-temperature routes in solution is advantageous, giving an intimate atomic mix and the ability to tailor molecules for decomposition.[7] These precursors guarantee a dispersion of the metal source at the molecular level and provide uniform reaction sites for conversion to the desired metal oxide film.

Low-temperature chemical vapor deposition (CVD) routes to metal oxide films have been previously studied.[8] Small changes in the molecular architecture of the ligands can alter the oligomerization, volatility, and mass transport of the materials.[9]

The difficulty in obtaining mixed-metal precursors of the desired stoichiometry is well documented; therefore, we have initiated a study on the use of separate precursors to form CSG (Ceria Supported Gadolinia). Previous researchers have pre-

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Table 1. Crystal Data and Refinement Results[a] for {[Gd(tmhd)₃]₂} (1), [Gd(tmhd)₃(monoglyme)] (2), {[Gd(tmhd)₃]₂(tetraglyme)} (5), and {[Gd(tmhd)₃]₂(heptaglyme)} (6)

	1	2	5	6
formula	$C_{66}H_{114}Gd_2O_{12}$	$C_{37}H_{67}GdO_8$	$C_{76}H_{136}Gd_2O_{17}$	$C_{82}H_{148}Gd_2O_{20}$
mol wt	1414.07	797.16	1636.35	1768.50
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
cell dimens				
a, Å	12.228(2)	10.814(2)	11.934(2)	11.773(2)
b, Å	27.615(2)	12.141(3)	19.478(4)	18.712(3)
c, Å	21.843(1)	16.534(2)	20.508(10)	21.610(3)
α, deg	90	83.897(9)	99.25(1)	90
β, deg	105.27(6)	88.196(12)	106.94(2)	103.53(1)
γ, deg	90	71.852(11)	104.76(1)	90
V, Å³	7115.50(12)	2051.06(7)	4265.31(2)	4628.34(2)
Z	4	2	2	2
ϱ(calc), g cm⁻³	1.320	1.291	1.274	1.269
μ, mm⁻¹	1.901	1.660	1.599	1.482
transm coeff	0.893−1.118	0.939−1.057	0.964−1.111	0.884−1.112
R_1[b]	0.0558 (0.0307)[c]	0.0319 (0.0290)[c]	0.0539 (0.0369)[c]	0.0391 (0.0265)[c]
wR_2[b]	0.1034 (0.0757)[c]	0.0778 (0.0729)[c]	0.1306 (0.1079)[c]	0.0840 (0.0672)[c]

[a] T = 150 K; λ = 0.710 69 Å. [b] $R_1 = \Sigma(\Delta F)/\Sigma F_o$, $wR_2 = [\Sigma\{w(\Delta(F^2))^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$, $w = 1/[\sigma^2(F_o)^2]$. [c] The values in parentheses were calculated for data with $I > 2\sigma(I)$ only.

pared several complexes of cerium(III) and -(IV) with ligands such as $N(SiMe_3)_2$,[10,11] various alcohols,[12−19] and β-diketonates,[20−24] but these materials were not found to be suitable as CVD precursors. In general, the metal alkoxides are poor CVD precursors because of their low volatility, thermal stability, and vapor pressure; the β-diketonates are better and their CVD properties can be further improved by the use of tailored molecular precursor synthesis.[25] In these studies, we have utilized a series of glymes to improve the general precursor properties of several lanthanide β-diketonate complexes.

The chemistry of the Gd alkoxides is poorly developed, and it has been shown that the compounds formally described as $[Ln(OPr^i)_3]_x$ are oxo-bridged aggregates.[26−28] A range of anhydrous β-diketonates and their respective aqua complexes have also been studied.[6,29]

Several adducts of the complex $Gd_2(tmhd)_6$ ({[Gd(tmhd)₃]$_n$-$(CH_3(OCH_2CH_2)_mOCH_3)$} where $n = 1$, $m = 1$, 2 and $n = 2$, $m = 3$, 4, 7) have been synthesized, using a low-temperature route,

and are described in this paper. The molecular materials have been evaluated by sublimation, TGA, and DSC as precursors for APCVD coatings of $Ce_{0.9}Gd_{0.1}O_{1.95}$ thick electrolyte films for SOFCs.

Experimental Section

All manipulations were carried out under normal laboratory conditions, unless otherwise specified. All hydrocarbon solvents were rigorously predried and then distilled over sodium metal by standard techniques. Elemental analyses were performed by the Microanalytical Service of Imperial College. Gadolinium was determined complexometrically by using cyclohexanediaminetetraacetic acid as the complexing agent and xylenol orange as indicator. The melting points were measured under nitrogen in sealed capillaries and are uncorrected values.

Infrared spectra were recorded on a Perkin-Elmer FT IR 1720 spectrometer as either Nujol or hexachlorobutadiene mulls between 25 × 4 mm CsI plates. The samples were protected from the atmosphere by an O-ring-sealed Presslok holder (available from Aldrich Chemicals).

Mass spectra were run on a Kratos MS30 using the instrument in electron impact positive mode at the Royal School of Pharmacy Mass Spectrometry Service, University of London.

Cryoscopic measurements were performed in freshly distilled benzene under anaerobic conditions using an electronically controlled thermistor based apparatus connected to a Flatbed chart recorder. All results are an average of at least three measurements.

Controlled thermal analyses of the complexes were investigated using a Polymer Laboratories 1500H simultaneous thermal analyzer, controlled by a 486DX-33 PC. The weight of the samples investigated was between 10 and 25 mg. The measurements were carried out in alumina crucibles under an atmosphere of flowing (25 cm³ min⁻¹) dry nitrogen gas, using heating rates of 5 °C min⁻¹.

Gadolinium oxide was donated by Rhone-Poulenc, Manchester, U.K. Gadolinium chloride was prepared by dissolution of the oxide in 8 M hydrochloric acid. The crystallized hydrated chloride was refluxed overnight in trimethylchlorosilane to reduce the water content. The white powder was dried at 80 °C under vacuum for 48 h and used without further purification. 2,2,6,6−Tetramethyl-3,5-heptanedione and mono-, di-, tri-, tetra-, and heptaglyme were obtained from Inorgtech of Mildenhall, Suffolk, U.K. The glymes were dried over 4-Å molecular sieves prior to use. Nujol and hexachlorobutadiene were obtained from Aldrich and dried over 4-Å molecular sieves prior to use.

Syntheses. (a) [Gd₂(tmhd)₆] (1). To a solution of NaOH pellets (1.00 g, 25.0 mmol) in MeOH (20 cm³) was slowly added tmhd-H (5.25 cm³, 25.0 mmol), and the mixture was stirred for 15 min. Separately, $GdCl_3$ (2.20 g, 8.3 mmol) dissolved in MeOH (20 cm³) was added dropwise to the above solution. The resulting mixture was stirred for 1 h and then stripped to dryness using a rotary evaporator. The off-white residue was extracted with hot *n*-hexane (3 × 20 mL

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for [{Gd(tmhd)$_3$}$_2$] (1)

	x	y	z	$U_{eq}{}^a$		x	y	z	$U_{eq}{}^a$
Gd(1)	2075.0(1)	1464.5(1)	3207.3(1)	17.2(1)	C(33)	−1606(4)	443(2)	3105(2)	33(1)
Gd(2)	465.8(1)	337.6(1)	2280.4(1)	17.9(1)	O(7)	1072(2)	−122(1)	3181(1)	25(1)
O(1)	3085(2)	1785(1)	2553(1)	24(1)	O(8)	1447(2)	−292(1)	2003(1)	24(1)
O(2)	3625(2)	1878(1)	3834(1)	25(1)	C(34)	1442(4)	−758(2)	3947(2)	36(1)
C(1)	4055(4)	2248(1)	1951(2)	28(1)	C(35)	1346(3)	−563(1)	3271(2)	26(1)
C(2)	3884(3)	2086(1)	2591(2)	22(1)	C(36)	1609(4)	−872(1)	2816(2)	29(1)
C(3)	4582(3)	2257(1)	3160(2)	26(1)	C(37)	1664(3)	−719(1)	2211(2)	24(1)
C(4)	4446(3)	2130(1)	3757(2)	24(1)	C(38)	2021(4)	−1070(2)	1749(2)	31(1)
C(5)	5308(3)	2287(1)	4369(2)	28(1)	C(39)	2646(6)	−744(4)	4324(3)	114(4)
C(6)	4946(4)	2647(2)	2010(2)	38(1)	C(40)	764(8)	−426(3)	4267(3)	132(4)
C(7)	2917(4)	2430(2)	1540(2)	38(1)	C(41)	928(9)	−1255(3)	3929(3)	117(4)
C(8)	4433(5)	1800(2)	1649(3)	46(1)	C(42)	3140(5)	−884(2)	1654(3)	58(2)
C(9)	5852(5)	1831(2)	4697(3)	55(2)	C(43)	2132(5)	−1591(2)	1977(3)	53(2)
C(10)	6238(4)	2623(2)	4257(2)	46(1)	C(44)	1120(4)	−1051(2)	1120(2)	45(1)
C(11)	4678(4)	2554(2)	4782(2)	47(1)	O(9)	−1202(2)	614(1)	1635(1)	24(1)
O(3)	2444(2)	1073(1)	4179(1)	26(1)	O(10)	−866(2)	−292(1)	2113(1)	27(1)
O(4)	1220(2)	1928(1)	3822(1)	26(1)	C(45)	−2841(3)	793(2)	810(2)	29(1)
C(12)	3146(4)	903(2)	5283(2)	37(1)	C(46)	−2130(3)	441(1)	1292(2)	23(1)
C(13)	2499(4)	1226(2)	4732(2)	29(1)	C(47)	−2503(3)	−27(2)	1359(2)	28(1)
C(14)	1988(4)	1654(2)	4871(2)	32(1)	C(48)	−1875(3)	−366(1)	1794(2)	26(1)
C(15)	1347(3)	1973(2)	4413(2)	28(1)	C(49)	−2385(4)	−853(2)	1916(2)	31(1)
C(16)	746(4)	2420(2)	4599(2)	36(1)	C(50)	−3848(3)	562(2)	339(3)	50(1)
C(17)	3926(5)	564(2)	5061(3)	55(1)	C(51)	−2068(4)	1022(2)	443(2)	45(1)
C(18)	2268(5)	616(2)	5519(3)	66(2)	C(52)	−3257(4)	1186(2)	1188(2)	45(1)
C(19)	3874(5)	1202(2)	5834(3)	64(2)	C(53)	−2437(6)	−850(2)	2595(3)	66(2)
C(20)	1267(5)	2863(2)	4376(2)	57(2)	C(54)	−3602(4)	−929(2)	1495(3)	57(2)
C(21)	−498(4)	2387(2)	4261(3)	60(2)	C(55)	−1642(5)	−1251(2)	1789(4)	63(2)
C(22)	890(6)	2455(2)	5317(3)	67(2)	O(11)	1033(2)	686(1)	1442(1)	24(1)
O(5)	721(2)	1887(1)	2451(1)	27(1)	O(12)	2312(2)	726(1)	2692(1)	21(1)
O(6)	301(2)	1006(1)	2943(1)	24(1)	C(56)	1954(3)	756(2)	619(2)	27(1)
C(23)	−805(4)	2425(2)	2036(2)	31(1)	C(57)	1985(3)	683(1)	1318(2)	24(1)
C(24)	−307(3)	1971(1)	2414(2)	27(1)	C(58)	3013(3)	599(1)	1792(2)	22(1)
C(25)	−968(3)	1672(1)	2710(2)	27(1)	C(59)	3142(3)	606(1)	2434(2)	21(1)
C(26)	−636(3)	1228(1)	2979(2)	25(1)	C(60)	4239(3)	456(1)	2905(2)	27(1)
C(27)	−1310(3)	957(2)	3375(2)	31(1)	C(61)	3125(4)	725(2)	495(2)	43(1)
C(28)	−62(4)	2848(2)	2316(3)	55(2)	C(62)	1207(4)	362(2)	239(2)	45(1)
C(29)	−752(5)	2339(2)	1356(2)	50(1)	C(63)	1428(4)	1249(2)	420(2)	43(1)
C(30)	−2020(4)	2533(2)	2042(3)	45(1)	C(64)	5182(4)	338(2)	2584(2)	45(1)
C(31)	−534(4)	913(2)	4044(2)	50(1)	C(65)	4653(3)	851(2)	3400(2)	32(1)
C(32)	−2401(4)	1227(2)	3387(3)	49(1)	C(66)	3984(4)	4(2)	3245(2)	44(1)

^{a} U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

portions), and the extracts were reduced to dryness to give a crude off-white solid. The product was recrystallized from hot *n*-hexane to give fine needles suitable for X-ray structural studies; yield 5.71 g (97% based on Gd). Mp: 176−177 °C. Anal. Calcd for Gd$_2$C$_{66}$H$_{114}$O$_{12}$: Gd, 22.24; C, 56.05; H, 8.14. Found: Gd, 22.0; C, 56.9; H, 8.3. Sublimation (5 × 10^{-3} Torr; °C): 110−148. MW: calcd, 1414.3; found, 1350 ± 70 (by freezing point depression in benzene).

(b) [Gd(tmhd)$_3$(monoglyme)] (2). The complex [Gd$_2$(tmhd)$_6$] (1.00 g, 0.7 mmol) was suspended in *n*-hexane (20 cm^3), and dimethoxyethane (0.05 cm^3, 1.4 mmol) was added; the reaction mixture was stirred for 1 h. The resulting solution was placed at −23 °C, and the complex crystallized within 2 days; yield 1.0 g (89% based on Gd). Mp: with evidence of dissolution in glyme, 117−130 °C. Anal. Calcd for GdC$_{37}$H$_{67}$O$_8$: Gd, 19.72; C, 55.74; H, 8.49. Found: Gd, 19.4; C, 55.9; H, 8.6. Sublimation (5 × 10^{-3} Torr): complex 1 was found on the cold finger (see Results and Discussion). MW: calcd, 797.29; found, 765 ± 75 (by freezing point depression in benzene).

(c) [Gd(tmhd)$_3$(diglyme)] (3). The complex [Gd$_2$(tmhd)$_6$] (1.00 g, 0.7 mmol) was dissolved in warm *n*-hexane (30 cm^3), and to this was added diglyme (0.20 cm^3, 1.6 mmol). The resulting solution was stirred for 30 min and then stripped to dryness to yield a yellow oil which solidified upon heating under vacuum and yielded an off-white solid. The complex was recrystallized from *n*-hexane; yield 1.12 g (94% based on Gd). Mp: 77−78 °C. Anal. Calcd for GdC$_{39}$H$_{71}$O$_9$: Gd, 18.69; C, 55.67; H, 8.52. Found: Gd, 18.8; C, 56.0; H, 8.5. Sublimation (5 × 10^{-3} Torr): complex 1 was found on the cold finger (see Results and Discussion). MW: calcd, 841.35; found 770 ± 75 (by freezing point depression in benzene).

(d) [{Gd(tmhd)$_3$}$_2$(triglyme)] (4). The complex [Gd$_2$(tmhd)$_6$] (1.00 g, 0.7 mmol) was dissolved in warm *n*-hexane (40 cm^3), and to this was added 0.26 cm^3 (1.5 mmol) of triglyme. The reaction conditions

and workup were as for complex 3. The evaporation of the solvent yielded a colorless oil, which was left undisturbed at room temperature and crystallized over a period of 3 days in quantitative yield. Mp: 119−121 °C. Anal. Calcd for Gd$_2$C$_{74}$H$_{132}$O$_{16}$: Gd, 19.75; C, 55.81; H, 8.37. Found: Gd, 19.2; C, 55.7; H, 8.2. Sublimation (5 × 10^{-3} Torr; °C): 110−135. MW: calcd, 1592.56; found, 1420 ± 60 (by freezing point depression in benzene).

(e) [{Gd(tmhd)$_3$}$_2$(tetraglyme)] (5). To a suspension of 1 (0.71 g, 0.5 mmol) in *n*-hexane (10 cm^3) was added tetraglyme (0.22 cm^3, 1.0 mmol). The reaction conditions and workup were as for complex 3. The colorless oil, which was formed after the evaporation of the solvent, was crystallized over a period of 2 weeks in the form of large blocks. Yield: 0.64 g (78% based on Gd). Mp: 91 °C. Anal. Calcd for Gd$_2$C$_{76}$H$_{136}$O$_{17}$: Gd, 19.22; C, 55.77; H, 8.39. Found: Gd, 19.2; C, 55.5; H, 8.2. Sublimation (5 × 10^{-3} Torr; °C): 85−165. MW: calcd, 1636.62; found, 1580 ± 40 (by freezing point depression in benzene).

(f) [{Gd(tmhd)$_3$}$_2$(heptaglyme)] (6). The complex [Gd$_2$(tmhd)$_6$] (0.70 g, 0.5 mmol) was suspended in *n*-hexane (10 cm^3), heptaglyme (0.35 cm^3, 1.0 mmol) was added, and the reaction mixture was stirred for 1 h. The reaction conditions and workup were as for complex 3. The colorless oil, which was formed after the evaporation of the solvent, was crystallized over a period of 3 h in the form of large cubes. Yield: 0.80 g (91% based on Gd). Mp: 82−84 °C. Anal. Calcd for Gd$_2$C$_{82}$H$_{148}$O$_{20}$: Gd, 17.78; C, 55.68; H, 8.43. Found: Gd, 17.2; C, 55.6; H, 8.4. Sublimation (5 × 10^{-3} Torr; °C): 75−130. MW: calcd, 1768.80; found, 1655 ± 80 (by freezing point depression in benzene).

X-ray Structural Determinations of Complexes 1, 2, 5, and 6. The unit cell parameters and intensity data were obtained at 150 K

(30) Darr, J. A.; Drake, S. R.; Hursthouse, M. B.; Malik, K. M. A. *Inorg. Chem.* **1993**, *32*, 5704.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [{Gd(tmhd)$_3$}$_2$] (1)

Gd(1)−O(4)	2.296(3)	Gd(1)−O(1)	2.298(3)
Gd(1)−O(3)	2.318(3)	Gd(1)−O(5)	2.321(3)
Gd(1)−O(2)	2.324(3)	Gd(1)−O(12)	2.383(3)
Gd(1)−O(6)	2.446(4)	O(1)−C(2)	1.270(4)
O(2)−C(4)	1.269(4)	O(3)−C(13)	1.266(5)
O(4)−C(15)	1.266(5)	O(5)−C(24)	1.259(5)
O(6)−C(26)	1.320(5)	O(6)−Gd(2)	2.386(3)
Gd(2)−O(8)	2.282(3)	Gd(2)−O(9)	2.283(4)
Gd(2)−O(7)	2.293(3)	Gd(2)−O(11)	2.330(3)
Gd(2)−O(10)	2.343(3)	Gd(2)−O(12)	2.447(4)
O(7)−C(35)	1.265(5)	O(8)−C(37)	1.268(4)
O(9)−C(46)	1.277(5)	O(10)−C(48)	1.265(5)
O(11)−C(57)	1.263(5)	O(12)−C(59)	1.326(4)
O(4)−Gd(1)−O(1)	123.44(11)	O(4)−Gd(1)−O(3)	74.55(11)
O(1)−Gd(1)−O(3)	137.91(11)	O(4)−Gd(1)−O(5)	77.68(11)
O(1)−Gd(1)−O(5)	76.32(12)	O(3)−Gd(1)−O(5)	144.71(10)
O(4)−Gd(1)−O(2)	78.96(12)	O(1)−Gd(1)−O(2)	71.88(11)
O(3)−Gd(1)−O(2)	75.97(11)	O(5)−Gd(1)−O(2)	119.39(12)
O(4)−Gd(1)−O(12)	152.06(7)	O(1)−Gd(1)−O(12)	83.33(8)
O(3)−Gd(1)−O(12)	90.84(8)	O(5)−Gd(1)−O(12)	104.26(8)
O(2)−Gd(1)−O(12)	121.10(9)	O(4)−Gd(1)−O(6)	85.08(12)
O(1)−Gd(1)−O(6)	129.87(10)	O(3)−Gd(1)−O(6)	85.49(11)
O(5)−Gd(1)−O(6)	70.74(12)	O(2)−Gd(1)−O(6)	158.14(9)
O(12)−Gd(1)−O(6)	69.88(8)	C(2)−O(1)−Gd(1)	137.9(2)
C(4)−O(2)−Gd(1)	137.9(3)	C(13)−O(3)−Gd(1)	131.8(3)
C(15)−O(4)−Gd(1)	134.4(3)	C(24)−O(5)−Gd(1)	130.6(3)
C(26)−O(6)−Gd(2)	127.5(2)	C(26)−O(6)−Gd(1)	118.3(2)
Gd(2)−O(6)−Gd(1)	109.41(11)	O(8)−Gd(2)−O(9)	122.50(11)
O(8)−Gd(2)−O(7)	74.50(10)	O(9)−Gd(2)−O(7)	138.46(10)
O(8)−Gd(2)−O(11)	79.60(10)	O(9)−Gd(2)−O(11)	77.24(12)
O(7)−Gd(2)−O(11)	143.78(10)	O(8)−Gd(2)−O(10)	77.68(13)
O(9)−Gd(2)−O(10)	71.37(12)	O(7)−Gd(2)−O(10)	77.17(11)
O(11)−Gd(2)−O(10)	121.45(11)	O(8)−Gd(2)−O(6)	152.11(8)
O(9)−Gd(2)−O(6)	84.93(8)	O(7)−Gd(2)−O(6)	88.12(8)
O(11)−Gd(2)−O(6)	104.35(8)	O(10)−Gd(2)−O(6)	120.12(9)
O(8)−Gd(2)−O(12)	86.13(12)	O(9)−Gd(2)−O(12)	131.91(11)
O(7)−Gd(2)−O(12)	82.46(11)	O(11)−Gd(2)−O(12)	70.81(11)
O(10)−Gd(2)−O(12)	156.70(9)	O(6)−Gd(2)−O(12)	69.82(8)
C(35)−O(7)−Gd(2)	132.7(3)	C(37)−O(8)−Gd(2)	133.5(2)
C(46)−O(9)−Gd(2)	138.5(2)	C(48)−O(10)−Gd(2)	138.1(3)
C(57)−O(11)−Gd(2)	130.3(2)	C(59)−O(12)−Gd(1)	128.1(2)
C(59)−O(12)−Gd(2)	118.0(2)	Gd(1)−O(12)−Gd(2)	109.49(11)

using a Delft Instruments FAST TV area detector diffractometer and graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å), by following previously described procedures.[30] The crystal data are summarized in Table 1. Number of data collected and unique data obtained after processing were as follows: (1) 36 216 ($-11 \leq h \leq 16$, $-36 \leq k \leq 36$, $-19 \leq l \leq 29$; $2.28 \leq \theta \leq 30.06°$), 17 809 unique; (2) 7467 ($-11 \leq h \leq 12$, $-14 \leq k \leq 13$, $-17 \leq l \leq 18$; 2.06 $\leq \theta \leq 25.07°$) collected, 5745 unique; (5) 13 432 ($-9 \leq h \leq 13$, $-23 \leq k \leq 23$, $-22 \leq l \leq 24$; $2.15 \leq \theta \leq 25.57°$) collected, 11 743 unique; (6) 14 246 ($-11 \leq h \leq 13$, $-13 \leq k \leq 21$, $-25 \leq l \leq 24$; $2.18 \leq \theta \leq 25.58°$) collected, 7136 unique. The data were corrected for Lorentz and polarization effects and also for absorption (DIFABS).[31] The structures were solved *via* heavy atom procedures (SHELX-S)[32] and refined on F_o^2 by full-matrix least squares (SHELXL-93)[33] using all unique data. Refinement of the structures of **1** and **6** proceeded smoothly with all nonhydrogen atoms anisotropic and hydrogen atoms in idealized positions with U_{iso} tied to the U_{eq} of their parent carbons. In the structure of **2**, one *tert*-butyl group was disordered between two orientations; the relevant carbons were assigned partial occupancy and refined anisotropically along with the other non-hydrogen atoms. All hydrogen atoms in this structure were also included in idealized positions with U_{iso} tied to the U_{eq} of their parents. The structure of **5** showed varied degrees of disorder involving one −CH$_2$CH$_2$− group in the tetraglyme and nine *tert*-butyl methyl groups. Some of the

(31) Walker N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158, adapted for FAST Geometry by A. Karaulov, University of Wales College of Cardiff, 1990.
(32) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.
(33) Sheldrick, G. M. SHELXL-93: Program for Crystal Structure Refinement, University of Göttingen, Germany, 1993.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for [Gd(tmhd)$_3$(monoglyme)] (2)

	x	y	z	$U_{eq}{}^a$
Gd(1)	1063.0(2)	4950.0(1)	2821.7(1)	14.9(6)
O(1)	2355(2)	6085(2)	2365(2)	21(1)
O(2)	−335(2)	6759(2)	2260(1)	19(1)
C(1)	3474(4)	7400(3)	1816(2)	25(1)
C(2)	2207(4)	7112(3)	2021(2)	19(1)
C(3)	999(4)	7925(3)	1839(2)	21(1)
C(4)	−216(4)	7727(3)	1963(2)	18(1)
C(5)	−1473(3)	8728(3)	1757(2)	22(1)
C(6)	4345(4)	6430(3)	1335(3)	46(1)
C(7)	3280(4)	8572(3)	1305(3)	33(1)
C(8)	4146(4)	7400(4)	2617(3)	40(1)
C(9)	−1414(4)	9322(3)	901(2)	34(1)
C(10)	−1627(4)	9615(3)	2390(3)	33(1)
C(11)	−2643(4)	8268(3)	1818(3)	33(1)
O(3)	2485(2)	3728(2)	2009(1)	21(1)
O(4)	−179(2)	4456(2)	1871(1)	19(1)
C(12)	3770(3)	2397(3)	1131(2)	19(1)
C(13)	2439(3)	3106(3)	1440(2)	17(1)
C(14)	1282(3)	3066(3)	1121(2)	21(1)
C(15)	26(4)	3746(3)	1337(2)	19(1)
C(16)	−1145(3)	3642(2)	893(2)	22(1)
C(17)	4562(4)	3234(3)	918(3)	38(1)
C(18)	3703(4)	1755(4)	398(3)	40(1)
C(19)	4445(4)	1494(3)	1826(3)	38(1)
C(20)^b	−1011(5)	3942(4)	−31(3)	39(1)
C(21)^b	−1185(5)	2382(3)	1027(3)	44(1)
C(22)^b	−2416(4)	4483(4)	1181(3)	47(2)
C(20')^c	−1017(36)	3108(19)	80(8)	39(1)
C(21')^c	−1771(18)	2981(21)	1547(14)	44(1)
C(22')^c	−2084(22)	4893(10)	738(26)	47(2)
O(6)	763(2)	3207(2)	3454(2)	20(1)
O(5)	2758(2)	4071(2)	3748(2)	22(1)
C(23)	4839(4)	2753(3)	4149(2)	28(1)
C(24)	3401(4)	2998(3)	3915(2)	21(1)
C(25)	2851(4)	2092(3)	3915(2)	21(1)
C(26)	1562(4)	2239(3)	3703(2)	18(1)
C(27)	1071(4)	1168(3)	3736(2)	20(1)
C(28)	5653(4)	1479(4)	4151(3)	49(1)
C(29)	5431(4)	3453(4)	3505(3)	50(1)
C(30)	4883(5)	3171(5)	4973(3)	70(2)
C(31)	1585(4)	571(3)	2959(2)	32(1)
C(32)	−411(4)	1555(3)	3727(2)	27(1)
C(33)	1579(4)	296(3)	4481(3)	39(1)
O(7)	−998(2)	5395(2)	3707(2)	23(1)
O(8)	856(2)	6347(2)	3925(2)	25(1)
C(34)	−2084(4)	5153(3)	3388(2)	32(1)
C(35)	−1365(4)	6478(3)	4068(3)	31(1)
C(36)	−208(4)	6575(3)	4478(2)	32(1)
C(37)	1980(4)	6529(3)	4251(3)	33(1)

^{a} U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. ^{b,c} Atoms in the disordered ^{t}Bu group. Partial occupancies: (b) = 0.884(4); (c) 0.116(4).

disordered carbons were refined successfully with anisotropic displacement parameters, but others were refined isotropically. The C−Me distances in the disordered *tert*-butyl groups were also constrained at 1.540(5) Å, because "free" refinement resulted in unacceptable bond lengths. The hydrogen atoms on the "isotropic" disordered carbons were ignored; the remaining hydrogens were included as in other cases. Final R$_1$/wR$_2$ values were 0.0558/0.1034 for (**1**) (17 809 data, 757 parameters), 0.0319/0.0778 for (**2**) (5745 data, 448 parameters), 0.0539/0.1306 for (**5**) (11 743 data, 910 parameters), and 0.0391/0.0840 for (**6**) (7136 data, 488 parameters).

Coordinates of the non-hydrogen atoms (including the site occupancies of the disordered carbons and U_{eq}/U_{iso}), and selected bond lengths and angles are given in Tables 2−9 for compounds **1**, **2**, **5** and **6**. All calculations were performed on a 486DX2/66 personal computer. Sources of atomic scattering factors were as in SHELXL-93.[33] The diagrams were drawn by the program SNOOPI.[34]

(34) Davies, K. SNOOPI: Program for Crystal Structure Drawing, University of Oxford, 1983.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for [Gd(tmhd)₃(monoglyme)] (**2**)

|			
Gd(1)−O(1)	2.309(2)	Gd(1)−O(2)	2.357(2)
Gd(1)−O(3)	2.290(2)	Gd(1)−O(4)	2.338(2)
Gd(1)−O(5)	2.336(3)	Gd(1)−O(6)	2.369(2)
Gd(1)−O(7)	2.571(2)	Gd(1)−O(8)	2.579(2)
O(1)−C(2)	1.279(4)	O(2)−C(4)	1.268(4)
O(3)−C(13)	1.280(4)	O(4)−C(15)	1.267(4)
O(5)−C(24)	1.277(4)	O(6)−C(26)	1.259(4)
O(7)−C(35)	1.439(4)	O(7)−C(34)	1.425(5)
O(8)−C(36)	1.424(4)	O(8)−C(37)	1.432(5)
O(1)−Gd(1)−O(2)	72.86(8)	O(1)−Gd(1)−O(4)	18.43(8)
O(1)−Gd(1)−O(5)	83.72(8)	O(1)−Gd(1)−O(6)	152.26(8)
O(1)−Gd(1)−O(7)	131.17(7)	O(1)−Gd(1)−O(8)	75.36(8)
C(2)−O(1)−Gd(1)	138.0(2)	O(2)−Gd(1)−O(6)	134.87(8)
O(2)−Gd(1)−O(7)	73.69(8)	O(2)−Gd(1)−O(8)	74.76(8)
O(3)−Gd(1)−O(1)	79.52(8)	O(3)−Gd(1)−O(2)	120.43(8)
O(3)−Gd(1)−O(4)	72.81(8)	O(3)−Gd(1)−O(5)	80.39(8)
O(3)−Gd(1)−O(6)	83.91(8)	O(3)−Gd(1)−O(7)	149.03(8)
O(3)−Gd(1)−O(8)	144.83(8)	O(4)−Gd(1)−O(2)	75.90(8)
O(4)−Gd(1)−O(6)	76.77(8)	O(4)−Gd(1)−O(7)	85.95(8)
O(4)−Gd(1)−O(8)	141.46(8)	O(5)−Gd(1)−O(4)	140.28(7)
O(5)−Gd(1)−O(2)	143.80(8)	O(5)−Gd(1)−O(6)	71.63(8)
O(5)−Gd(1)−O(7)	104.19(8)	O(5)−Gd(1)−O(8)	72.81(8)
O(6)−Gd(1)−O(7)	69.18(7)	O(6)−Gd(1)−O(8)	107.97(8)
O(7)−Gd(1)−O(8)	62.15(8)	C(4)−O(2)−Gd(1)	136.5(2)
C(13)−O(3)−Gd(1)	130.0(2)	C(26)−O(6)−Gd(1)	131.8(2)
C(34)−O(7)−Gd(1)	115.9(2)	C(35)−O(7)−Gd(1)	116.8(2)
C(36)−O(8)−Gd(1)	121.4(2)	C(37)−O(8)−Gd(1)	121.3(2)

Results and Discussion

Synthesis and Physical Properties. The complexes of Gd with β-diketonates, e.g. tmhd-H, hfpd-H (1,1,1,5,5,5-hexafluoropentane-2,4-dione), and acac-H, were targeted as MOCVD precursors due to their volatility, stability, and ease of preparation. These ligands in combination with glymes have been chosen, since they should block aggregate growth and hence increase the volatility and mass transport of the complexes. Tailoring of the precursors *via* judicious choice of O-donor ligands and β-diketones should be such that a hydrocarbon sheath encapsulates the metal center. This ensures organic solvent solubility and also that moisture will not be able to attack the metal center. Previously[35,36] we have shown that the reaction between hydrated lanthanide β-diketonates and triglyme led to the formation of water-free products with better mass transport properties than those of the parent compounds. In this paper, we have expanded this study by using a wider range of glymes.

The reaction of hydrated gadolinium chloride with the sodium salt of tmhd-H in an aqueous/alcoholic media initially yields the hydrated β-diketonate complex [Gd(tmhd)₃(H₂O)]. Extraction into *n*-hexane yields the homoleptic complex [Gd₂(tmhd)₆] (**1**) as shown in eq i.

$$2GdCl_3 + 6Na(tmhd) \xrightarrow[-6NaCl]{MeOH/water}$$
$$2[Gd(tmhd)_3(H_2O)] \xrightarrow[-2H_2O]{n\text{-hexane}} [Gd_2(tmhd)_6] \quad (i)$$
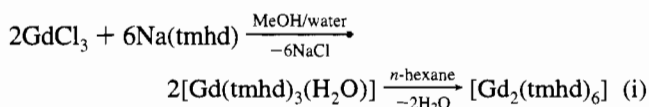
This complex reacted readily with a wide range of O-donor-based Lewis bases and in particular long-chain glyme ligands, i.e. Me(OCH₂CH₂)ₘOMe (where *m* = 1, 2, 3, 4, and 7) as shown in eq ii.

$$[Gd_2(tmhd)_6] + L\text{-}L \rightarrow [\{Gd(tmhd)_3\}_n(L\text{-}L)] \quad (ii)$$
$$n = 1, 2$$
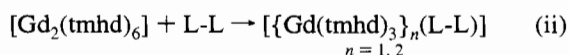
The reactions of **1** with monoglyme and diglyme yielded [Gd-(tmhd)₃(L-L)] **2** and **3** and with triglyme, tetraglyme, and heptaglyme yielded the dimeric complexes [{(tmhd)₃Gd}₂(L-

L)] (**4−6**).[37] The reaction with the longer chain glyme ligands formally yields dimeric complexes where the individual Gd-(tmhd)₃ moieties are held together by bridging glyme ligands. Attempts to prepare a trimeric complex, utilizing six of the eight oxygen donors available in heptaglyme, or to use higher excesses of glymes in the preparations of complexes **4−6** for the isolation of monomeric species were not successful.

There are several synthetic features that are noteworthy: (a) this synthetic strategy of using a preformed metal β-diketonate complex (either anhydrous or hydrated) leads to water-free products with improved mass transport properties compared with those of the parent β-diketonate; (b) the coordinative saturation of the metal center by the multidentate chelate and β-diketonate leads to *air- and moisture-stable* precursors of known stoichiometry; this has great potential since L-L may be varied with the use of either O or N functionalized chelating ligands; (c) the designed synthesis of volatile discrete molecular metal organics does not depend on using sterically hindered ligands, e.g. C₆H₂Buᵗ₃O.

Compounds **1−6** all have excellent solubilities in a wide range of organic solvents (i.e. aromatic and aliphatic hydrocarbons, halogenated hydrocarbons, alcohols, and ethers). This pronounced solubility even in non-polar aliphatic hydrocarbon solvents (i.e. *n*-hexane) can be attributed to their coordinative saturation and the presence of a hydrocarbon surface on the molecule. A further important observation (especially if these materials are to have industrial applications) is their excellent stability to both air and moisture.

Apart from complex **2** which decomposes on melting, the compounds melt clearly at relatively low temperatures and more significantly at a lower temperature than the parent complex (**1**). The melting points appear to be reduced from that of the homoleptic parent compound (171−172 °C) to those of the adducts with the higher glymes (89−91 °C for complex **5** and 80−82 °C for complex **6**). Obviously the diglyme adduct, complex **3**, melts at a lower temperature (77−78 °C) than the other complexes because it is a monomer. The melting points of the compounds **3−6** are also lower than that of the hydrated complex [Gd(tmhd)₃(H₂O)] (183−184 °C).[38] These data may be compared with those for the mono(pyridine) adducts [Ln-(tmhd)₃(py)] (mp for the Gd(III) complex: 134−135 °C) which are also lower than those for [Ln(tmhd)₃(H₂O)]. With the more bulky nitrogen Lewis base pyrazine, mono adducts are also formed, e.g. [Ln(tmhd)₃(C₄H₄N₂)], but their melting points are similar to those of the hydrated β-diketonate compounds.[39]

The sublimation studies clearly separate the adducts in two distinct groups: the "lower glyme adducts" (complexes **2** and **3**) which after sublimation give the parent homoleptic compound (**1**) on the cold finger and the "higher glyme adducts" (complexes **4−6**) which sublime intact at lower temperatures ([{Gd(tmhd)₃}₂(triglyme)], 110−135 °C; [{Gd(tmhd)₃}₂(tetraglyme)], 85−165 °C; [{Gd(tmhd)₃}₂(heptaglyme)], 75−130 °C (at 5 × 10⁻³ Torr)) than the parent complex (**1**) (110−148 °C at 5 × 10⁻³ Torr). It appears that DME and diglyme ligands

(35) Drake, S. R.; Lyons, A.; Otway, D. J.; Slawin, A. M. Z.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1993**, 2379.

(36) Drake, S. R.; Hursthouse, M. B.; Malik, K. M. A.; Miller, S. A. S.; Otway, D. J. *Inorg. Chem.* **1993**, *32*, 4464.

(37) All physical measurements for the complexes were done on materials obtained as described in the Experimental Section. It was observed that, in the case of **4−6**, the ratio of the reactants in the reaction mixtures affects the crystallization time and the purity of the products. When only 0.5 equiv of glyme is used, the complexes are crystallized as off-white solids after the evaporation of the solvent. Recrystallization is essential to ensure the purity of the products. With 2 equiv of the corresponding glyme in the reaction mixture the resulting oils crystallized very slowly (i.e. in 1 month) to give the products which were washed with methanol to remove excess glyme. The products obtained by different routes as above gave satisfactory analyses.

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Table 6. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for [{Gd(tmhd)$_3$}$_2$(tetraglyme)] (5)

	x	y	z	$U_{eq}{}^a$		x	y	z	$U_{eq}{}^a$
Gd(1)	4500(1)	4808(1)	2432(1)	12(1)	C(44)^b	7404(16)	11828(9)	4629(9)	45(4)^d
O(1)	2623(4)	4948(2)	1836(2)	18(1)	C(42′)^c	8590(16)	11478(9)	3834(7)	38(4)^d
O(2)	3516(4)	3871(2)	1362(2)	19(1)	C(43′)^c	8252(16)	11754(8)	5169(5)	37(4)^d
C(1)	449(6)	4736(4)	1477(3)	22(2)	C(44′)^c	7113(14)	11617(10)	4004(8)	48(5)^d
C(2)	1568(6)	4476(4)	1473(3)	18(2)	O(9)	7104(5)	9465(3)	2267(3)	33(1)
C(3)	1409(6)	3775(3)	1080(3)	15(1)	O(10)	4957(5)	8276(3)	1717(2)	33(1)
C(4)	2388(6)	3523(4)	1030(3)	19(2)	C(45)	7989(9)	10012(5)	1494(4)	52(3)
C(5)	2134(7)	2779(4)	517(4)	25(2)	C(46)	6923(8)	9448(4)	1621(4)	33(2)
C(6)	−793(7)	4159(4)	1055(4)	38(2)	C(47)	5894(9)	8984(5)	1067(4)	43(2)
C(7)	563(8)	4976(5)	2256(4)	38(2)	C(48)	4957(8)	8429(4)	1128(4)	32(2)
C(8)	571(7)	5420(4)	1176(4)	33(2)	C(49)	3845(8)	7954(4)	472(4)	41(2)
C(9)	2713(9)	2933(5)	−43(4)	51(3)	C(50)^b	7576(23)	9993(13)	702(5)	72(7)^d
C(10)	749(8)	2337(5)	147(5)	57(3)	C(51)^b	9232(12)	10272(10)	2113(7)	45(5)^d
C(11)	2802(9)	2327(4)	947(4)	53(3)	C(50′)^c	8140(27)	9766(15)	781(8)	90(8)^d
O(3)	3305(4)	3892(2)	2756(2)	20(1)	C(51′)^c	9202(18)	9872(18)	1862(15)	113(10)^d
O(4)	4177(4)	5369(2)	3428(2)	17(1)	C(52)	7840(15)	10773(5)	1679(10)	174(9)
C(12)	1965(7)	3031(4)	3128(4)	22(2)	C(53)	4230(11)	7389(6)	53(5)	81(4)
C(13)	2771(6)	3823(3)	3211(3)	15(1)	C(54)	2819(9)	7485(7)	681(5)	103(5)
C(14)	2884(6)	4424(4)	3739(3)	19(2)	C(55)^b	2984(17)	8370(10)	132(10)	54(5)^d
C(15)	3578(6)	5150(4)	3821(3)	17(2)	C(55′)^c	3510(18)	8417(8)	−55(7)	42(4)^d
C(16)	3667(6)	5770(3)	4436(3)	18(2)	O(11)	4688(4)	9728(2)	2357(2)	25(1)
C(17)	2739(8)	2526(4)	3056(4)	32(2)	O(12)	3745(5)	8494(3)	2789(2)	26(1)
C(18)	1532(7)	2948(4)	3754(4)	28(2)	C(56)	3314(7)	10271(4)	1704(3)	23(2)
C(19)	844(7)	2834(4)	2463(4)	38(2)	C(57)	3567(7)	9660(4)	2073(3)	20(2)
C(20)	3132(8)	5489(4)	4982(4)	32(2)	C(58)	2604(7)	9120(4)	2117(4)	25(2)
C(21)	5049(7)	6212(4)	4827(4)	29(2)	C(59)	2711(7)	8577(4)	2477(3)	21(2)
C(22)	2982(7)	6270(4)	4121(4)	26(2)	C(60)	1558(6)	8054(3)	2538(4)	27(2)
O(5)	5643(4)	3987(2)	2542(2)	22(1)	C(61)	2070(8)	9996(5)	1097(4)	44(2)
O(6)	6584(4)	5479(2)	3145(2)	17(1)	C(62)	3292(9)	10895(4)	2277(4)	43(2)
C(23)	6939(7)	3242(4)	2750(4)	24(2)	C(63)	4360(8)	10582(5)	1442(4)	42(2)
C(24)	6712(6)	3996(4)	2881(3)	18(2)	C(64)^e	930(16)	8500(8)	2911(9)	44(4)
C(25)	7659(6)	4623(4)	3338(4)	23(2)	C(65)^e	629(13)	7640(10)	1790(5)	61(5)
C(26)	7548(6)	5325(4)	3444(3)	17(1)	C(66)^e	1870(14)	7462(7)	2903(8)	39(4)
C(27)	8650(6)	5978(4)	3950(4)	22(2)	C(64′)^f	1448(18)	7256(5)	2235(10)	40(5)
C(28)	6774(10)	3007(5)	1968(4)	53(3)	C(65′)^f	1855(18)	8154(12)	3339(5)	63(7)
C(29)	5933(9)	2690(4)	2902(6)	57(3)	C(66′)^f	352(13)	8224(13)	2224(13)	71(8)
C(30)	8220(7)	3256(4)	3201(4)	40(2)	O(13)	7169(5)	5239(3)	608(2)	24(1)
C(31)	8181(7)	6439(4)	4427(4)	30(2)	O(14)	5480(4)	5153(2)	1516(2)	19(1)
C(32)	9174(7)	6440(4)	3491(4)	28(2)	O(17)	7977(5)	8883(3)	3435(3)	30(1)
C(33)	9698(7)	5767(4)	4431(4)	34(2)	C(67)	7390(8)	5157(5)	−51(4)	36(2)
Gd(2)	5801(1)	9023(1)	2881(1)	17(1)	C(68)	6252(7)	4630(4)	618(3)	24(2)
O(7)	5985(5)	8975(2)	4063(2)	25(1)	C(69)	6185(6)	4688(4)	1347(3)	18(2)
O(8)	6910(5)	10179(2)	3607(2)	24(1)	C(70)	6043(7)	5908(4)	1598(4)	27(2)
C(34)	6470(7)	9095(4)	5308(4)	23(2)	C(71)	5137(8)	6295(4)	1694(4)	31(2)
C(35)	6547(6)	9404(3)	4663(3)	16(1)	O(15)	4865(4)	6154(2)	2308(2)	17(1)
C(36)	7254(7)	10143(4)	4783(3)	25(2)	O(16)	5851(4)	7734(2)	2969(2)	23(1)
C(37)	7376(6)	10498(4)	4252(3)	20(2)	C(72)	4137(7)	6592(4)	2510(4)	24(2)
C(38)	8101(7)	11317(4)	4433(3)	40(2)	C(73)	4907(7)	7218(3)	3128(3)	21(2)
C(39)	5915(9)	9551(5)	5732(4)	46(2)	C(74)^e	7047(13)	7589(7)	3046(7)	25(3)^d
C(40)	5637(9)	8310(4)	5062(4)	41(2)	C(75)^e	7982(13)	8159(8)	3641(8)	30(3)^d
C(41)	7729(9)	9137(6)	5769(5)	59(3)	C(74′)^f	7021(15)	7675(9)	3391(9)	21(3)^d
C(42)^b	9257(12)	11513(11)	4229(10)	55(5)^d	C(75′)^f	7997(16)	8184(9)	3235(9)	27(4)^d
C(43)^b	9354(10)	11448(9)	5018(7)	35(4)^d	C(76)	9078(8)	9465(5)	3727(7)	82(4)

^{a} U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. ^{b,c} Atoms in the disordered groups. Partial occupancies: (b) 0.500(4); (c) 0.500(4). ^{d} U_{iso}. ^{e,f} Atoms in the disordered groups. Partial occupancies: (e) 0.550(4); (f) 0.450(4).

in 2 and 3 are labile under the sublimation conditions and the complexes decompose to form initially the monomeric coordinatively unsaturated "Gd(tmhd)$_3$" species which then rearrange readily to give the dinuclear compound 1.

The synthesis of complex 5 has been scaled up successfully using a modification of the method described here. The product was used for the successful deposition of gadolinia by means of CVD. Complex 5 has been found to be thermally stable (i.e., it does not decompose after heating at 200 °C for at least 3 h). These results will be published in a later paper.

The paramagnetism of the gadolinium(III) ion in these complexes has precluded solution NMR studies. The cryoscopic molecular weight determinations indicate that these molecules retain their identities in solution and the glyme ligands do not dissociate

Description of the Structures. Single-crystal X-ray studies were undertaken on complexes 1, 2, 5, and 6 to unambiguously

identify the structural composition and to determine whether all of the potential O-donor sites are bound to the gadolinium metal centers. Unfortunately single crystals suitable for X-ray work could not be obtained for 3 and 4.

(a) **X-ray Structure of [Gd$_2$(tmhd)$_6$] (1).** The crystal structure of 1 consists of discrete dimeric molecules of [Gd$_2$-(tmhd)$_6$] held together by van der Waals forces and is shown in Figure 1. It possesses an approximate 2-fold axis of symmetry, relating the two {Gd(tmhd)$_3$} moieties forming the dimer based on two bridging tmhd ligands. Each gadolinium atom is bonded to two terminal chelating tmhd ligands in addition to the bridging tmhd ligand. The gadolinium atom is thus bonded to seven oxygen atoms with its coordination geometry best described as a distorted monocapped trigonal prism. The capping atoms are O(3) and O(7), on the faces defined by O(2), O(4), O(6), O(12) and O(8), O(10), O(6), O(12), respectively, for the two polyhedra around the metal

Table 7. Selected Bond Lengths (Å) and Angles (deg) for [{Gd(tmhd)₃}₂(tetraglyme)] (**5**)

Gd(1)−O(3)	2.301(4)	Gd(1)−O(1)	2.326(4)
Gd(1)−O(4)	2.340(4)	Gd(1)−O(5)	2.348(4)
Gd(1)−O(2)	2.376(4)	Gd(1)−O(6)	2.376(5)
Gd(1)−O(14)	2.576(4)	Gd(1)−O(15)	2.613(4)
O(1)−C(2)	1.275(8)	O(2)−C(4)	1.260(8)
O(3)−C(13)	1.280(7)	O(4)−C(15)	1.277(8)
O(5)−C(24)	1.257(8)	O(6)−C(26)	1.270(8)
Gd(2)−O(8)	2.301(5)	Gd(2)−O(11)	2.319(4)
Gd(2)−O(12)	2.344(5)	Gd(2)−O(9)	2.356(5)
Gd(2)−O(10)	2.360(5)	Gd(2)−O(7)	2.389(5)
Gd(2)−O(16)	2.559(4)	Gd(2)−O(17)	2.616(5)
O(7)−C(35)	1.251(8)	O(8)−C(37)	1.256(8)
O(9)−C(46)	1.274(9)	O(10)−C(48)	1.288(9)
O(11)−C(57)	1.256(8)	O(12)−C(59)	1.278(8)
O(13)−C(68)	1.401(8)	O(13)−C(67)	1.443(7)
O(14)−C(70)	1.412(8)	O(14)−C(69)	1.451(7)
O(17)−C(75′)	1.36(2)	O(17)−C(76)	1.392(9)
O(17)−C(75)	1.536(14)	C(71)−O(15)	1.439(7)
O(15)−C(72)	1.458(7)	O(16)−C(74′)	1.46(2)
O(16)−C(73)	1.459(8)	O(16)−C(74)	1.49(2)

O(3)−Gd(1)−O(1)	84.4(2)	O(3)−Gd(1)−O(4)	73.0(2)
O(1)−Gd(1)−O(4)	83.3(2)	O(3)−Gd(1)−O(5)	77.6(2)
O(1)−Gd(1)−O(5)	144.8(2)	O(4)−Gd(1)−O(5)	118.8(2)
O(3)−Gd(1)−O(2)	77.8(2)	O(1)−Gd(1)−O(2)	71.6(2)
O(4)−Gd(1)−O(2)	143.0(2)	O(5)−Gd(1)−O(2)	75.2(2)
O(3)−Gd(1)−O(6)	122.0(2)	O(1)−Gd(1)−O(6)	142.8(2)
O(4)−Gd(1)−O(6)	80.8(2)	O(5)−Gd(1)−O(6)	71.4(2)
O(2)−Gd(1)−O(6)	134.9(2)	O(3)−Gd(1)−O(14)	146.76(14)
O(1)−Gd(1)−O(14)	94.2(2)	O(4)−Gd(1)−O(14)	139.96(14)
O(5)−Gd(1)−O(14)	85.3(2)	O(2)−Gd(1)−O(14)	70.4(2)
O(6)−Gd(1)−O(14)	77.5(2)	O(3)−Gd(1)−O(15)	143.93(14)
O(1)−Gd(1)−O(15)	70.5(2)	O(4)−Gd(1)−O(15)	78.59(13)
O(5)−Gd(1)−O(15)	136.9(2)	O(2)−Gd(1)−O(15)	115.92(14)
O(6)−Gd(1)−O(15)	73.46(14)	O(14)−Gd(1)−O(15)	63.17(12)
C(2)−O(1)−Gd(1)	131.4(4)	C(4)−O(2)−Gd(1)	130.7(4)
C(13)−O(3)−Gd(1)	139.0(4)	C(15)−O(4)−Gd(1)	135.4(4)
C(24)−O(5)−Gd(1)	138.2(4)	C(26)−O(6)−Gd(1)	136.3(4)
O(8)−Gd(2)−O(11)	78.3(2)	O(8)−Gd(2)−O(12)	119.3(2)
O(11)−Gd(2)−O(12)	73.1(2)	O(8)−Gd(2)−O(9)	79.3(2)
O(11)−Gd(2)−O(9)	83.2(2)	O(12)−Gd(2)−O(9)	144.8(2)
O(8)−Gd(2)−O(10)	146.4(2)	O(11)−Gd(2)−O(10)	81.6(2)
O(12)−Gd(2)−O(10)	79.1(2)	O(9)−Gd(2)−O(10)	71.9(2)
O(8)−Gd(2)−O(7)	71.9(2)	O(11)−Gd(2)−O(7)	118.9(2)
O(12)−Gd(2)−O(7)	77.2(2)	O(9)−Gd(2)−O(7)	137.9(2)
O(10)−Gd(2)−O(7)	141.7(2)	O(8)−Gd(2)−O(16)	133.5(2)
O(11)−Gd(2)−O(16)	146.9(2)	O(12)−Gd(2)−O(16)	81.0(2)
O(9)−Gd(2)−O(16)	108.4(2)	O(10)−Gd(2)−O(16)	73.5(2)
O(7)−Gd(2)−O(16)	73.4(2)	O(8)−Gd(2)−O(17)	78.43(13)
O(11)−Gd(2)−O(17)	147.01(13)	O(12)−Gd(2)−O(17)	139.41(12)
O(9)−Gd(2)−O(17)	69.74(14)	O(10)−Gd(2)−O(17)	106.38(14)
O(7)−Gd(2)−O(17)	74.77(13)	O(16)−Gd(2)−O(17)	63.23(11)
C(35)−O(7)−Gd(2)	136.3(4)	C(37)−O(8)−Gd(2)	139.5(4)
C(46)−O(9)−Gd(2)	133.5(6)	C(48)−O(10)−Gd(2)	131.2(5)
C(57)−O(11)−Gd(2)	136.3(5)	C(59)−O(12)−Gd(2)	135.4(5)
C(70)−O(14)−Gd(1)	116.8(4)	C(69)−O(14)−Gd(1)	113.6(3)
C(75′)−O(17)−Gd(2)	113.1(7)	C(76)−O(17)−Gd(2)	124.4(4)
C(75)−O(17)−Gd(2)	116.1(6)	C(71)−O(15)−Gd(1)	116.2(3)
C(72)−O(15)−Gd(1)	121.3(4)	C(74′)−O(16)−Gd(2)	116.9(7)
C(73)−O(16)−Gd(2)	122.8(4)	C(74)−O(16)−Gd(2)	117.0(6)

Table 8. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å² $\times 10^3$) for [{Gd(tmhd)₃}₂(heptaglyme)] (**6**)

	x	y	z	$U_{eq}{}^a$
Gd(1)	4237.8(1)	1125.0(1)	2286.1(1)	20.2(8)
O(1)	3463(2)	1692(1)	3056(1)	27(1)
O(2)	2634(2)	1770(1)	1750(1)	31(1)
C(1)	2421(3)	2296(2)	3718(2)	29(1)
C(2)	2563(3)	2072(2)	3056(2)	27(1)
C(3)	1733(3)	2257(2)	2512(2)	31(1)
C(4)	1799(3)	2102(2)	1893(2)	27(1)
C(5)	802(3)	2319(2)	1322(2)	34(1)
C(6)	2100(4)	1625(2)	4043(2)	49(1)
C(7)	3580(4)	2597(3)	4098(2)	49(1)
C(8)	1473(4)	2864(3)	3698(2)	52(1)
C(9)	−7(5)	1698(3)	1162(3)	91(2)
C(10)	138(5)	2970(3)	1466(3)	93(2)
C(11)	1327(5)	2516(4)	774(3)	110(3)
O(3)	2738(2)	317(1)	2375(1)	30(1)
O(4)	3744(2)	460(1)	1360(1)	29(1)
C(12)	987(3)	−338(2)	2265(2)	32(1)
C(13)	1939(3)	2(2)	1978(2)	26(1)
C(14)	1915(3)	−66(2)	1334(2)	31(1)
C(15)	2819(3)	154(2)	1054(2)	28(1)
C(16)	2763(4)	27(2)	346(2)	39(1)
C(17)	−99(4)	−564(3)	1764(2)	57(2)
C(18)	631(4)	197(3)	2719(2)	47(1)
C(19)	1535(4)	−995(2)	2639(3)	53(1)
C(20)	1701(5)	−387(4)	−1(2)	91(2)
C(21)	2875(6)	736(3)	43(3)	88(2)
C(22)	3833(5)	−424(3)	309(2)	74(2)
O(5)	5041(2)	1851(1)	1635(1)	27(1)
O(6)	5864(2)	1727(1)	2931(1)	27(1)
C(23)	5801(3)	2751(2)	1078(2)	31(1)
C(24)	5768(3)	2364(2)	1698(2)	25(1)
C(25)	6500(3)	2563(2)	2274(2)	29(1)
C(26)	6540(3)	2230(2)	2855(2)	26(1)
C(27)	7463(3)	2437(2)	3461(2)	30(1)
C(28)	4550(4)	2981(3)	767(2)	52(1)
C(29)	6214(5)	2220(3)	649(2)	67(2)
C(30)	6578(4)	3417(3)	1167(2)	57(1)
C(31)	8142(3)	3118(2)	3378(2)	42(1)
C(32)	8312(4)	1817(2)	3635(2)	51(1)
C(33)	6860(4)	2567(2)	4005(2)	42(1)
O(7)	6059(2)	380(2)	2196(1)	37(1)
O(8)	5025(2)	245(2)	3151(1)	35(1)
O(9)	6097(2)	280(2)	4552(1)	36(1)
O(10)	8580(2)	347(2)	4972(1)	41(1)
C(34)	6520(4)	410(3)	1652(2)	62(2)
C(35)	6471(5)	−117(4)	2637(3)	89(2)
C(36)	6104(4)	−107(3)	3207(2)	54(1)
C(37)	4478(3)	148(2)	3670(2)	33(1)
C(38)	5017(3)	593(2)	4230(2)	35(1)
C(39)	6708(4)	720(2)	5054(2)	38(1)
C(40)	7807(3)	338(2)	5380(2)	39(1)
C(41)	9624(3)	−33(2)	5229(2)	41(1)

 ^{a} U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

centers. The structure of the dimer is derived from two such capped prisms sharing an edge [O(6)···O(12)]. The two gadolinium atoms are separated by 3.944(2) Å. The four terminally chelating tmhd ligands are quite symmetrically bonded to the Gd atoms as indicated by the nearly equal Gd−O distances of 2.282(3)−2.343(3) Å (average 2.306 Å) with the C−O distances also nearly equal at 1.265(5)−1.277(5) Å (average 1.268 Å). In contrast, the bridging tmhd ligands are quite asymmetrically bonded as indicated by the Gd−O distances of 2.321(3) Å [Gd(1)−O(5)], 2.446(4) Å [Gd(1)−O(6)], 2.330(3) Å [Gd(2)−O(11)], and 2.447(4) Å [Gd(2)−O(12)]. The additional bonds that the bridging ligands form with the second gadolinium atom in the dimer have lengths of 2.386(3) Å [Gd(2)−O(6)] and 2.383(3) Å [Gd(1)−O(12)],

showing that the bridge bonds are also asymmetric. The asymmetry in the bridging tmhd ligands is reflected in and is consistent with the observed lengthening of the C=O bonds involving the two μ_2-O atoms [1.326(4), 1.320(5) Å] compared with the nonbridging O atoms [1.263(5), 1.259(5) Å]. Further, the bridging tmhd ligands show considerably larger folding about the O···O axis (*ca.* 40°) compared with the terminal ligands (5−19°) as a consequence of the bridge formation.

The series of Ln₂(tmhd)₆ complexes (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy) are isostructural. Early photographic data on the Pr derivative[40] led to a poor *R* factor (*R* = 0.133), while an attempted structural study of the Y(III) analogue[41] (*R* = 0.18)

(40) Erasmus, C. S.; Boeyens, J. C. A. *Acta Crystallogr.* **1970**, *B26*, 1843.
(41) Gromilov, S. A.; Baidina, I. A.; Stabnikov, P. A.; Prokhorova, S. A.; Igumenov, I. K. *Z. Strukt. Khim.* **1993**, *34*, 163.
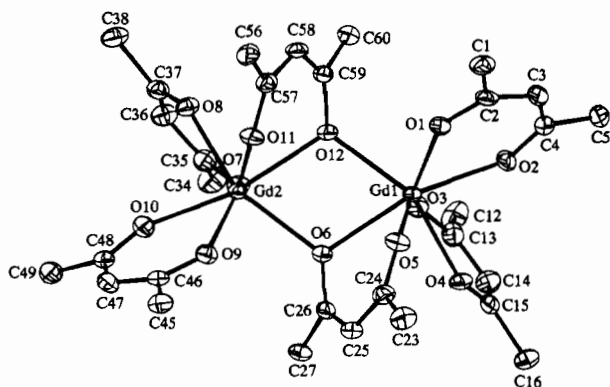
Figure 1. Molecular structure of [Gd₂(tmhd)₆] (**1**) showing the atom-numbering scheme. Atom O(7) is partially obscured by Gd(2). The *tert*-butyl methyl groups and the hydrogen atoms have been omitted for clarity.

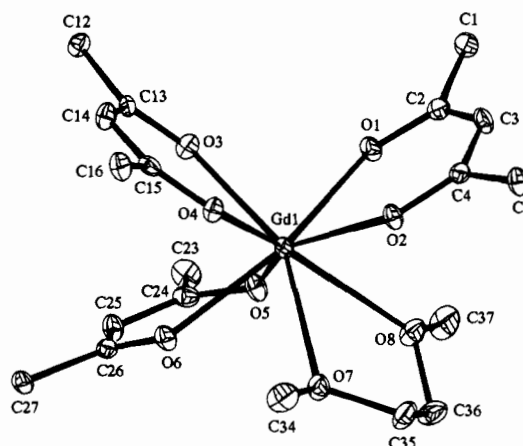**Figure 2.** Molecular structure of [Gd(tmhd)₃(monoglyme)] (**2**) showing the atom-numbering scheme. The *tert*-butyl methyl groups and the hydrogen atoms have been omitted for clarity.

Table 9. Selected Bond Lengths (Å) and Angles deg for [{Gd(tmhd)₃}₂(heptaglyme)] (**6**)

Gd(1)−O(1)	2.331(2)	Gd(1)−O(2)	2.311(3)
Gd(1)−O(3)	2.366(2)	Gd(1)−O(4)	2.313(3)
Gd(1)−O(5)	2.312(2)	Gd(1)−O(6)	2.372(3)
Gd(1)−O(7)	2.603(3)	Gd(1)−O(8)	2.500(3)
O(1)−C(2)	1.277(4)	O(2)−C(4)	1.261(4)
O(3)−C(13)	1.262(4)	O(4)−C(15)	1.271(4)
O(5)−C(24)	1.271(4)	O(6)−C(26)	1.269(4)
O(7)−C(34)	1.407(5)	O(7)−C(35)	1.338(6)
O(8)−C(36)	1.411(5)	O(8)−C(37)	1.430(4)
O(9)−C(38)	1.424(4)	O(9)−C(39)	1.416(5)
O(10)−C(40)	1.407(5)	O(10)−C(41)	1.416(5)
O(1)−Gd(1)−O(3)	78.95(9)	O(1)−Gd(1)−O(6)	76.22(9)
O(1)−Gd(1)−O(7)	139.78(9)	O(1)−Gd(1)−O(8)	84.54(9)
O(2)−Gd(1)−O(1)	73.17(9)	O(2)−Gd(1)−O(3)	80.58(9)
O(2)−Gd(1)−O(4)	80.57(9)	O(2)−Gd(1)−O(5)	77.91(9)
O(2)−Gd(1)−O(6)	119.98(10)	O(2)−Gd(1)−O(7)	146.40(9)
O(2)−Gd(1)−O(8)	146.64(8)	O(3)−Gd(1)−O(6)	140.41(9)
O(3)−Gd(1)−O(7)	107.90(10)	O(3)−Gd(1)−O(8)	70.84(9)
O(4)−Gd(1)−O(1)	143.26(8)	O(4)−Gd(1)−O(3)	71.67(9)
O(4)−Gd(1)−O(6)	140.23(8)	O(4)−Gd(1)−O(7)	72.06(9)
O(4)−Gd(1)−O(8)	105.46(10)	O(5)−Gd(1)−O(1)	116.83(9)
O(5)−Gd(1)−O(3)	147.60(9)	O(5)−Gd(1)−O(4)	81.08(9)
O(5)−Gd(1)−O(6)	71.92(9)	O(5)−Gd(1)−O(7)	78.92(9)
O(5)−Gd(1)−O(8)	135.16(8)	O(6)−Gd(1)−O(7)	74.46(9)
O(6)−Gd(1)−O(8)	76.49(9)	O(8)−Gd(1)−O(7)	62.29(9)
C(2)−O(1)−Gd(1)	135.8(2)	C(4)−O(2)−Gd(1)	136.6(2)
C(13)−O(3)−Gd(1)	134.0(2)	C(15)−O(4)−Gd(1)	134.8(2)
C(24)−O(5)−Gd(1)	137.7(2)	C(26)−O(6)−Gd(1)	136.2(2)
C(34)−O(7)−Gd(1)	121.7(3)	C(35)−O(7)−Gd(1)	119.1(3)
C(36)−O(8)−Gd(1)	122.7(2)	C(37)−O(8)−Gd(1)	120.9(2)
C(35)−O(7)−C(34)	118.5(3)	C(36)−O(8)−C(37)	115.9(3)
C(39)−O(9)−C(38)	111.8(3)	C(40)−O(10)−C(41)	112.2(3)

has shown similar molecular structure. The present data provide the first accurate description of the structure of this important group of compounds.

(b) X-ray Structure of [Gd(tmhd)₃(monoglyme)] (2). The crystal structure of **2** consists of monomeric molecules of [Gd-(tmhd)₃(DME)] held together by van der Waals forces, and the molecular structure, which is shown in Figure 2, is based on a square antiprismatic geometry. The gadolinium ion is chelated by all three tmhd ligands and DME (monoglyme). This structural type is quite common in lanthanide β-diketonate chemistry, and it has been described previously in [Ho(tmhd)₃-(4-pic)₂],[42] [La(acac)₃(H₂O)₂],[43] [Eu(tmhd)₃(py)₂],[44] [{Y(tmhd)₃}₂-(triglyme)],[36] and [{Eu(tmhd)₃}₂(triglyme)].[35] The Gd−O bond distances fall into two distinctly different groups: those to the
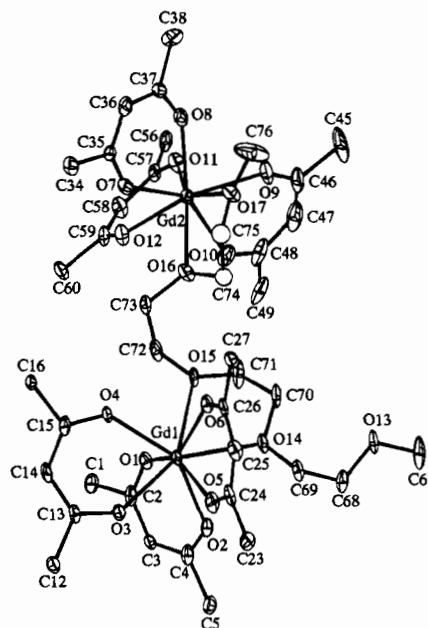
Figure 3. Molecular structure of [Gd₂(tmhd)₆(tetraglyme)] (**5**) showing the atom-numbering scheme. The *tert*-butyl methyl groups and the hydrogen atoms have been omitted for clarity.

β-diketonate ligands which lie in the range 2.290(2)−2.369(3) Å (average 2.333 Å) and those for the monoglyme, which are 2.571(3) and 2.579(3) Å (average 2.575 Å). The difference in the above mean values (0.242 Å) is about twice that expected on the basis of multiplicity of the C−O bonds in the two ligands, and this indicates that the Gd−O_ether bonds are relatively weaker than the Gd−O_β-diketone bonds. It is also observed that two O₂C₃ moieties are nearly coplanar with the metal (fold angles about the O⋯O axis 2.2 and 5.8°) while the third is considerably bent (fold angle about the O⋯O axis 27.20°) away from the DME ligand.

An important feature observed in the present structure is the asymmetry in the two M−O bonds connecting each tmhd ligand to the metal. The differences in these bonds are small (mean value 0.043 Å) but seem to be real since the longer M−O bond is always associated with carbonyl oxygen having a bond length ca. 0.014 Å shorter than the other. The two M−O_glyme bonds are nearly equal, which suggests that this ligand is symmetrically bonded to gadolinium.

Only four examples of X-ray structures of compounds with DME coordinated to lanthanide ions have previously been reported: the complex [Nd(OCH-*i*-Pr₂)₆(μ-DME)]_∞,[27] where monoglyme is acting as a bidentate bridging ligand, and the

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(43) Phillips, T.; Sands, D. E.; Wagner, W. P. *Inorg. Chem.* **1968**, *7*, 2295.
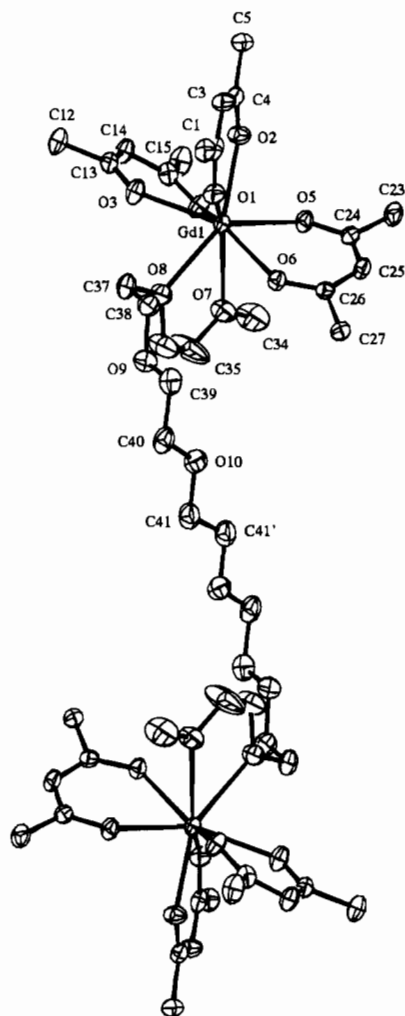(44) Cramer, R. E.; Sef, K. *J. Chem. Soc., Chem. Commun.* **1972**, 400.

Figure 4. Molecular structure of [Gd₂(tmhd)₆(heptaglyme)] (**6**) showing the atom-numbering scheme. The *tert*-butyl methyl groups and the hydrogen atoms have been omitted for clarity.

complexes {[(Me₃Si)₂N]₂Eu(DME)₂},[45] {[(Me₃Si)₂N]SmI(DME)-(THF)}₂,[46] and [Ce(NO₃)₃(DME)₂],[47] where DME is a bidentate chelating ligand. The average Gd–O$_{glyme}$ distances in complex **2** compare reasonably with the corresponding distances in the complexes above when the differences in oxidation state and coordination number are taken into account.[48]

(c) X-ray Structure of [{Gd(tmhd)₃}₂(tetraglyme)] (5). The crystal structure of **5** consists of dimeric molecules of [{Gd-(tmhd)₃}₂(tetraglyme)] held together by van der Waals forces. The molecular structure of **5** is shown in Figure 3. It consists of two {Gd(tmhd)₃} moieties linked together by tetraglyme with an unusual bridging bonding mode.

In this compound both the metal centers are eight-coordinate with distorted square antiprismatic geometries. Each gadolinium atom is bonded to six oxygen atoms belonging to three chelating tmhd ligands and two oxygen atoms belonging to tetraglyme. The Gd–O bond lengths can be separated into two groups: those to the β-diketonate ligands in the range 2.301(4)−2.389-(5) Å (average 2.345 Å) and those to the tetraglyme which are in the range 2.559(4)−2.616(5) Å (average 2.591 Å). The tmhd ligands are mostly asymmetrically bonded to the metal as shown by the differences in the two M–O bonds involving each ligand.

(45) Tilley, T. D.; Zalkin, A.; Andersen, R. A.; Templeton, D. H. *Inorg. Chem.* **1981**, *20*, 551.
(46) Evans, W. J.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 575.
(47) Gradeff, P. S.; Yunlu, K.; Deming, T. J.; Olofson, J. M.; Ziller, J. W.; Evans, W. J. *Inorg. Chem.* **1989**, *28*, 2600.
(48) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

The most interesting feature of complex **5** is that the glyme ligand bridges the two {Gd(tmhd)₃} moieties in an asymmetric and very unusual manner. Tetraglyme utilizes only four of its five available oxygen atoms for coordination. Bearing in mind that nine-coordination is not uncommon in Gd(III) chemistry[49] tetraglyme could have used all its five oxygens to give a dimeric structure with one eight- and one nine-coordinated gadolinium atom. A study of a space-filling model of **5** indicates that the coordination of an additional glyme oxygen center is not favorable because the three tightly held tmhd ligands and two of the glyme oxygen atoms coordinatively saturate the gadolinium metal center. In the case of the lanthanum, the corresponding complex [La(tmhd)₃(tetraglyme)] is monomeric and nine-coordinated with tetraglyme utilizing three oxygen atoms for coordination.[35] Obviously, the size of the central atom plays an important role in deciding the number of donors around it, with larger metal atoms favoring larger coordination numbers. It was shown recently that when two tmhd ligands are coordinated to a metal center of large radius, all five oxygen atoms of the tetraglyme can be coordinated to the metal, e.g. [Ba(tmhd)₂(tetraglyme)].[25]

(d) X-ray Structure of [{Gd(tmhd)₃}₂(heptaglyme)] (6). The crystal structure of **6** consists of dimeric molecules of [{Gd-(tmhd)₃}₂(heptaglyme)] held together by van der Waals forces. The molecular structure of **6**, shown in Figure 4, is centrosymmetric and consists of two {Gd(tmhd)₃} moieties linked together by one heptaglyme ligand. The center of symmetry lies in the middle (between carbons C(41) and C(41′)) of the heptaglyme moiety.

In this complex, in common with **2** and **5**, the metal centers are eight coordinate and have distorted square antiprismatic geometries. The gadolinium atoms are each bonded to six oxygen atoms belonging to three chelating tmhd ligands and to two terminal oxygen atoms belonging to the bridging heptaglyme. The Gd–O$_{tmhd}$ distances are in the range 2.311(2)−2.372(3) Å (average 2.334 Å), while the Gd–O$_{glyme}$ distances are 2.603(3) and 2.500(3) Å (average 2.552 Å). The tmhd ligands are again asymmetrically chelated to the metal, as observed in **1**, **2** and **5**, but the glyme is also asymmetric in the same manner as that observed in **5**.

Complex **6** is the first example of a compound with coordinated heptaglyme to be structurally characterized. The most interesting feature of this structure is the coordination mode of the glyme. Only the two end pairs of oxygens of the long polyether chain are utilized for coordination, leaving four oxygen atoms between the two {Gd(tmhd)₃} cores uncoordinated. The two oxygen atoms around the inversion center are in *anti* conformation, directing the two {Gd(tmhd)₃} cores to opposite sides of the chain.

Spectroscopic Characterization. (a) Infrared Spectra. Complexes **1**−**6** were studied as both Nujol and hexachlorobutadiene mulls between CsI windows. The IR spectra of complexes **2**−**6** reveal only one set of C⁼O and C⁼C stretches (C⁼O, at *ca.* 1590 and 1540 cm⁻¹; C⁼C, at *ca.* 1575 and 1505 cm⁻¹) and possibly indicate only one tmhd ligand environment in the complexes. This is in contrast with the parent compound (**1**), which has at least one extra peak, at 1553 cm⁻¹, which can be assigned to C⁼O stretching mode.[50,51]

Another difference between compound **1** and compounds **2**−**6** is the presence of the ν(C−O) bands of the glyme at *ca.* 1070 cm⁻¹ (this is a shift of approximately 70 cm⁻¹ over the free ligands). It was not possible to assign the ν(C−O) of the

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(50) Liang, C. Y.; Schimitsehek, E. J.; Trias, J. A. *J. Inorg. Nucl. Chem.* **1970**, *32*, 811.
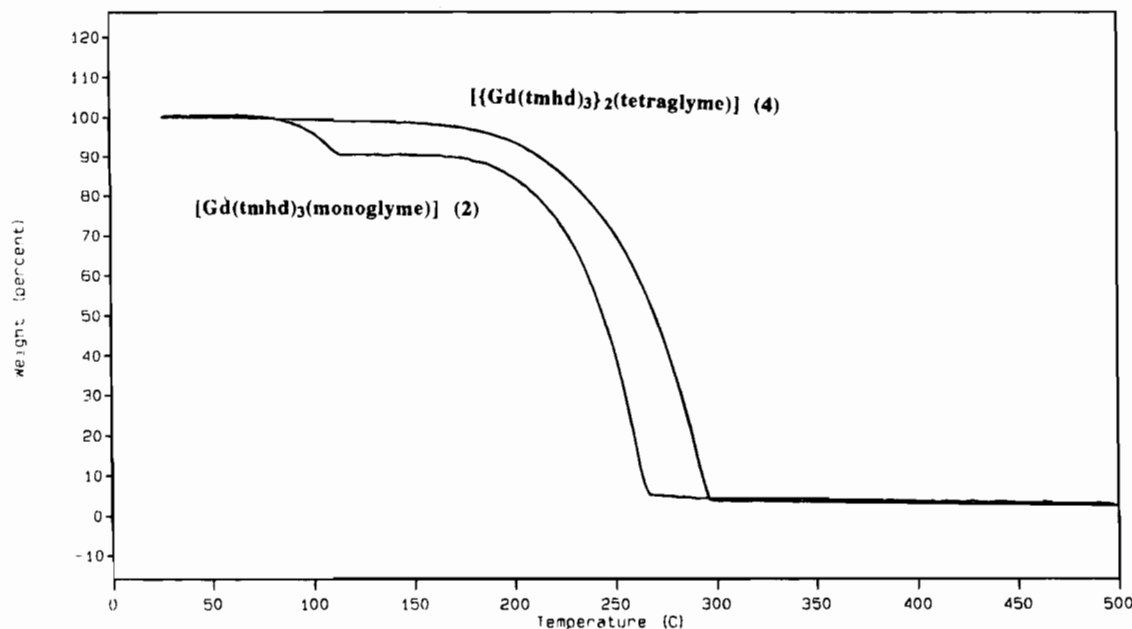(51) Dutt, N. K.; Sur, S.; Kahut, S. *J. Inorg. Nucl. Chem.* **1971**, *33*, 1717.

Figure 5. Thermal gravimetric analysis plots for compounds **2** and **4**.
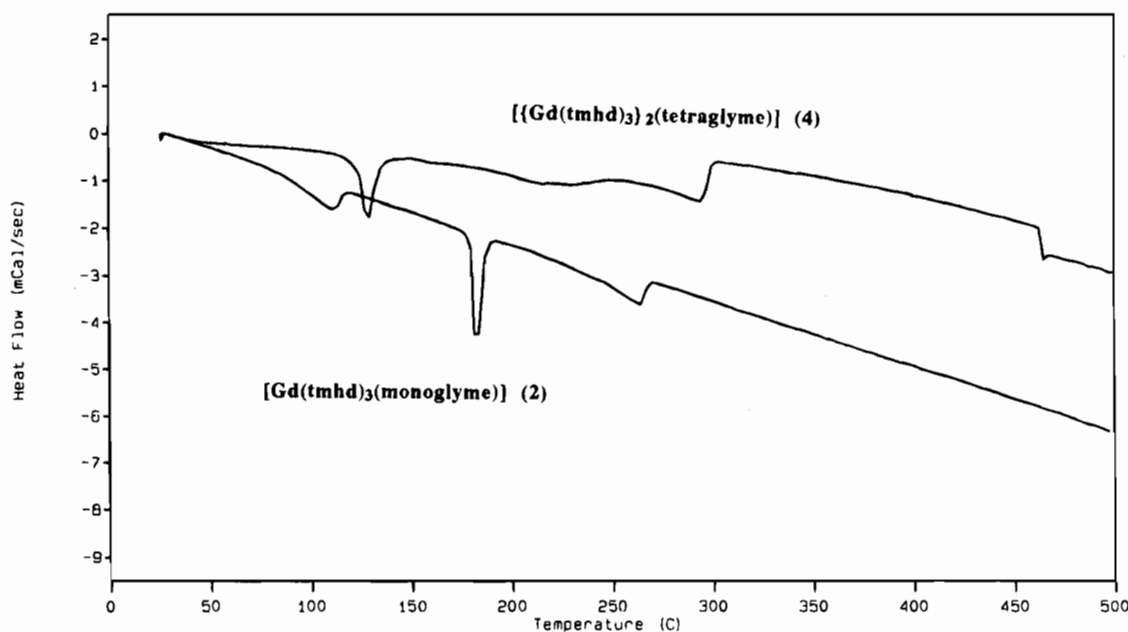

Figure 6. Differential scanning calorimetry curves for compounds **2** and **4**.

uncoordinated part of the glymes in complexes **3**, **5**, and **6** probably because they overlap with other vibrational modes. The metal−oxygen (tmhd) stretching frequencies are assigned at *ca.* 400 cm^{-1}, and our data are in good accord with previous work.[52]

(b) Mass Spectrometry. The mass spectral data (deposited as supplementary material) for complexes **1**, **3**−**5** reveal that there is no coordinated glyme present under the conditions present in the mass spectrometer. This behavior for the coordinated glyme has been previously noted by us for other lanthanide complexes.[53] The highest molecular mass ions observed for these complexes are due to the [Gd(tmhd)$_3$]$^+$ species at 706 amu. Other intense peaks observed included [Gd(tmhd)$_2$(Bu^{t}COCHCO)]$^+$ at 650 and [Gd(tmhd)$_2$]$^+$ at 523 amu, and below this, break-up of the tmhd groups was seen.

(52) Lee, H. Y.; Cleveland, F. F.; Ziomek, J. S.; Jorke, F. *Appl. Spectrosc.* **1972**, *26*, 251.
(53) Baxter, I.; Drake, S. R.; Hursthouse, M. B.; Lyons, A.; Malik, K. M. A.; Otway, D. J.; Plakatouras, J. C. Manuscript in preparation.

Although under high-vacuum conditions (10^{-8} Torr) these complexes dissociate to form the monomeric donor−Lewis base free complexes, Gd(tmhd)$_3$, these compounds may be used under atmospheric conditions very effectively under or low-vacuum (*ca.* 10^{-3} Torr) conditions as molecular precursors for Ln$_2$O$_3$.

In contrast to the above complexes **2** and **6** reveal molecular ions containing glyme ligands, e.g. [Gd$_2$(tmhd)$_6$(MeOCH$_2$CH$_2$OMe)$_2$]$^+$ at 1592 amu and [Gd$_2$(tmhd)$_6$(MeO(CH$_2$CH$_2$O)$_3$Me)]$^+$ at 1590 amu. These observations, particularly in the case of **2**, suggest that after the initial decomposition had occurred under the conditions of the mass spectrometry measurements, the resultant species aggregate in the gas phase to yield the dimeric complex [Gd$_2$(tmhd)$_6$(MeOCH$_2$CH$_2$OMe)$_2$]$^+$ at 1592 amu. Similarly, compound **6** also aggregates in the gas phase to yield [Gd$_2$(tmhd)$_5$(Bu^{t}COCHCOH)]$^+$ at 1356 amu, [Gd$_2$(tmhd)$_5$]$^+$ at 1230 amu, and [Gd$_2$(tmhd)(Bu^{t}COCHCOH)]$^+$ at 875 amu.

TGA/DSC Studies. TGA, DTA, and DSC give valuable information on the temperature required for pyrolysis of the

precursors. This information is vital if decomposition of precursors in the entry tubes prior to the reactor zone is to be avoided.

Both the homoleptic parent β-diketonate and the glyme-stabilized products were subjected to thermal analysis (TGA and DSC over the temperature range 20−600 °C). The results clearly showed that the addition of glyme ligands improves, from the CVD point of view, the properties of the adducts, especially for the longer glymes.

Representative TGA and DSC curves of complexes **2** and **4** are presented in Figures 5 and 6, respectively.

The TGA curve of complex **1** shows a one-step sublimation between 185 and 289 °C . A final residue of 2.0% indicates an almost quantitative sublimation. The DSC of **1** exhibits two endothermal processes. The first at 185.5 °C (-20.93 mcal mg^{-1}) corresponds well with the observed melting point of the complex. The second isotherm is very broad, sited between 242 and 290 °C (-13.48 mcal mg^{-1}), and corresponds to the large weight loss of 98.0% observed in the TGA (i.e. sublimation).

Complexes **2** and **3** are stable up to 84 and 119 °C, respectively. A weight loss of 9.8%, for **2**, between 84 and 117 °C is close to the calculated (11.3%) value for the loss of one DME molecule per gadolinium atom. A plateau is reached between 117−180 °C, and the thermal behavior of the intermediate product is almost identical to that of complex **1**. The DSC of **2** shows an irreversible broad endotherm at 111.3 °C (-9.07 mcal mg^{-1}), suggesting the loss of DME. The next sharp endotherm at 181.5 °C (-15.07 mcal mg^{-1}) corresponds to the melting point of the parent homoleptic compound, and the last broad endotherm centered at 264.4 °C (-7.81 mcal mg^{-1}) is due to the sublimation of the same complex. The diglyme adduct, **3** shows similar TGA behavior, but the DSC curve is different. After complex **3** has lost diglyme between 119 and 155 °C (weight loss: found, 17.6%, calcd, 16.0%), the intermediate product is stable up to 180 °C, and this then sublimes in the region 190−280 °C. The DSC curve of **3** shows the first sharp endotherm at 84.3 °C (-7.67 mcal mg^{-1}) which is reversible and is due to the melting of the intact complex. The following two endotherms, a very broad one centered at 138.5 °C and a sharp one centered at 165.5 °C (-13.63 mcal mg^{-1}), appear to be related to the loss of the diglyme, the latter corresponding very well to the boiling point of diglyme (162 °C).

The TGA of compounds **4−6** are quite straightforward; the compounds are stable up to *ca.* 200 °C and then they sublime in one step before 300 °C. In all cases, the final residue is less than 2.5% and indicates almost quantitative sublimation. The melting points of these compounds, shown as sharp endothermal peaks, are in agreement with the visually observed melting points [129.32 (-4.85), 101.12 (-6.87), and 86.36 °C (-6.44 mcal mg^{-1}), respectively]. The broad endotherms between 200 and 300 °C correspond to the sublimations of these products. The overall resemblance in the thermograms of these three complexes suggests that they probably have a similar structural framework.

Conclusions

The primary aims of this research are the production and characterization of new SOFC precursors and thick electrolyte

films of CSG by APCVD. The processes used may be studied by analyzing reaction components, stopping the reactions before completion, and altering reaction rates and stoichiometry to improve the thick films. This research should lead to CSG SOFC precursors, which will be amenable to use on the open bench, have the desired molecular nature, high volatility, and mass transport properties, and be effective low-temperature precursors.

This research describes for the first time adducts of {Gd-(tmhd)$_3$} with a variety of glyme ligands from monoglyme (two oxygen donors) to heptaglyme (eight oxygen donors). These complexes were readily synthesized from the parent tmhd complex and the glymes. The complexes described here have several properties pertinent to MOCVD. They are readily obtained as crystalline solids of known stoichiometry that are soluble in hydrocarbons (both aliphatic or aromatic) and air stable. It has been demonstrated that the longer chain glymes produce more stable complexes which have better mass transport properties.

The structural types observed here are in some cases unique (complexes **5** and **6**) and extend the structural chemistry of lanthanide β-diketonates. It appears that Gd(III) is coordinatively saturated by eight oxygen donors when bulky organic substituents (from the tmhd ligands) provide an effective shield against the incoming ligands. When hfpd (hfpd-H = 1,1,1,5,5,5-hexafluoropentane-2,4-dione) replaced tmhd in complex **1**, a tetrameric complex was formed with nine-coordinated gadolinium ions.[54] Although the coordination modes of the longer polyether ligands can be explained in terms of coordinative saturation and size of the central atom, more examples with structurally characterized complexes are essential for the complete understanding of their behavior.

The use of glyme ligands has reduced the conventional problems of oligomerization and subsequent low volatility. We consider that an important requirement in designing molecular precursors is that sufficient coordinative saturation be incorporated into both ligand and Lewis base chelate, such that a low molecular mass volatile monomer results.

Not only should careful design of such materials extend the metal−oxygen-based chemistry, but one can envisage the use of these complexes as a template for further reactivity with either lithium organometallics, to yield stabilized mixed alkaline rare earth organometallics, or other rare earth β-diketonates, to yield the as yet unexplored area of mixed-metal β-diketonates.

Supplementary Material Available: Tables S1−S16, containing full listings of crystal data, data collection and refinement parameters, bond lengths and angles, anisotropic displacement coefficients, and hydrogen atom parameters for compounds **1, 2, 5,** and **6,** and Tables S17 and S18, containing infrared spectroscopic and mass spectrometric details for **1−6** (34 pages). Ordering information is given on any current masthead page.

(54) Plakatouras, J. C.; Baxter, I.; Hursthouse, M. B.; Malik, K. M. A.; McAleese, J.; Drake, S. R. *J. Chem. Soc., Chem. Commun.* **1994,** 2455.