Inorg. Chem. **1994**, *33*, 1230–1233

An Unexpected Product Derived from the Reaction of $TbCl_3(H_2O)_6$ and $[Na(hfa)]_n$: Synthesis, Characterization, and X-ray Structure of $\{[Tb_2(hfa)_4(\mu_2\text{-}O_2CCF_3)_2(H_2O)_4][Tb(hfa)_3(H_2O)_2]_2 \cdot H_2O\}$ (hfa = $CF_3COCHCOCF_3$)

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Received July 20, 1993

Introduction

In recent years there have been considerable research developments in the chemistry of the lanthanide β-diketonates and alkoxides with many novel and important results obtained.[2] The primary driving force behind this research is the need to develop suitable molecular precursor technology for thin-film growth of both lanthanide and multimetallic oxides, i.e. $YBa_2Cu_3O_{7-x}$,[3] $LaCuO_2$,[4] and $Pb_2Sr_2LnCu_3O_{8-x}$.[5] These materials find application in the rapidly expanding area of electroceramics; examples include superconductors, piezoelectrics, Shottky devices, diffusion barriers, ferroelectrics, etc.[6] A wide variety of techniques have been used to prepare such materials and include hot isostactic pressing, ball milling, sintering, physical vapor deposition (PVD), and various sputtering techniques.[7] Metal oxide based ceramics have also been synthesized by classical "heat and bake" high-temperature routes.[8]

In contrast, chemical vapor deposition (CVD) processes offer a softer approach with a lower processing temperature and greater throwing power than alternative techniques. This process yields films by utilizing metal β-diketonates and alkoxides, which break down in the gas phase by well-established decomposition mechanisms. These materials also find application due to their high purity (>99.99%), well-defined stoichiometry, volatility, and mass transport properties.[9] Indeed, other workers have demonstrated the potential of lanthanide alkoxides and β-diketonates as low-temperature sources of Ln_2O_3 in multimetallic oxides.[10]

Lanthanide β-diketonates have been extensively reported and shown to exist as either Lewis base stabilized monomers, i.e. $M(thd)_3(L)_n$, or as dimeric or other oligomeric species.[11] The majority of these studies yielded hydrated metal β-diketonates.[12] Herein, we report the reaction of $[TbCl_3(H_2O)_6]$ with $[Na(hfa)]_n$ in aqueous media, which produces a compound in high, reproducible yield that is characterized by X-ray diffraction as $\{[Tb_2(hfa)_4(\mu_2\text{-}O_2CCF_3)_2(H_2O)_4][Tb(hfa)_3(H_2O)_2]_2 \cdot H_2O\}$.

Table 1. Crystallographic Data for **1**

chem formula	$C_{54}H_{26}F_{66}O_{32}Tb_4 \cdot H_2O$	fw	3094.4
a/Å	11.648(3)	space group	$P\bar{1}$
b/Å	12.844(3)	T/°C	20
c/Å	17.420(4)	λ/Å	0.710 73
α/deg	101.45(2)	D_c/g cm^{-3}	2.118
β/deg	104.24(2)	μ(Mo Kα)/cm^{-1}	30.79
γ/deg	98.06(2)	R^a	6.52
V/Å^3	2426.2(10)	$R_w{}^b$	7.05
Z	1		

[a] $R = \sum(F_o - F_c)/\sum(F_o)$. [b] $R_w = \sum w^{1/2}(F_o - F_c)/\sum w^{1/2}(F_o)$. The form of the weighting function is $w^{-1} = \sigma^2(F) + 0.0005F^2$.

Experimental Section

All manipulations were carried out under an atmosphere of dry (molecular sieves) argon or nitrogen using standard glovebox (Miller-Howe FF 160 with double recirculator system) and Schlenk techniques (using "greaseless" J. Young's joints/valves). The cyclohexane was rigorously predried and then distilled over sodium by standard techniques, and the methanol was dried and distilled over magnesium metal. Elemental analysis was performed by the microanalytical department of Imperial College. The melting point was measured under argon in a sealed capillary and is an uncorrected value.

Infrared spectra were recorded on a Perkin-Elmer FTIR 1720 spectrometer as either Nujol or hexachlorobutadiene mulls between 25 × 4 mm CsI plates. The Nujol and hexachlorobutadiene were both predried with 4-Å molecular sieves prior to use (and stored in the glovebox); 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 electron-impact positive ion mode at the Royal School of Pharmacy mass spectrometry service, University of London.

Controlled thermal analysis of the complex was investigated using a Polymer Laboratories 1500H simultaneous thermal analyzer, controlled by a Omni Pro 486DX-33 PC connected to a Ricoh 1200 laser printer. The weight of the sample investigated was 25 mg. The measurement was carried out in an alumina crucible under an atmosphere of flowing (25 mL/min) nitrogen gas, using a heating rate of 5 °C/min.

The hfa-H (hexafluoroacetylacetonate) and terbium chloride were obtained from Inorgtech, Mildenhall, Suffolk, U.K.

Preparation of $\{[Tb_2(hfa)_4(\mu_2\text{-}O_2CCF_3)_2(H_2O)_4][Tb(hfa)_3(H_2O)_2]_2 \cdot H_2O\}$ (1). Sodium hydroxide pellets (1.6 g, 40 mmol) were dissolved in methanol (10 mL), and hfa-H (9.1 g, 44 mmol, 10% excess) in MeOH (10 mL) was added in one aliquot with stirring to this solution. Hydrated $TbCl_3$ (3.5 g, 13 mmol) was then added in small portions and the solution stirred for a further 20 min. The reaction mixture was reduced in vacuo to yield an oil, distilled water (100 mL) was added, and the resulting solution was stirred for a further 5 min. The water was decanted to yield a green oil, which was subsequently washed with cyclohexane (50 mL). The cyclohexane was removed by decantation and the oil left to stand at 20 °C for 24 h to crystallize as large green crystals, which were filtered off. Yield: 5.0 g, 50%. Mp: desolvates at 64 °C, melts 132–136 °C. Anal. Found: C, 20.65; H, 0.81. Calc for $C_{54}H_{28}F_{66}O_{33}Tb_4$: C, 20.94; H, 0.90. IR (Nujol mull; ν, cm^{-1}): 3665 (w), 3451 (m, OH), 1649 (vs), 1619 (s), 1566 (s), 1537 (s), 1498 (s), 1260 (vs), 1207 (vs), 1151 (vs), 1097 (vs), 868 (w), 807 (s), 772 (w), 744 (m), 734 (m), 723 (w), 662 (s), 588 (s), 529 (m), 470 (w), 425 (w), 371 (w). IR (hexachlorobutadiene mull; ν, cm^{-1}): 3667 (w), 3451 (w, OH), 2926 (w), 2852 (w), 2782 (w), 1650 (m), 1634 (m), 1611 (vs), 1470 (m). MS (EI$^+$): 780, $[Tb(hfa)_3]^+$ (5%); 711, $[Tb(hfa)_2(CF_3COCHCO)]^+$ (65%); 573, $[Tb(hfa)_2]^+$ (47%); 523, $[Tb(hfa)(CF_3COCHCO)(F)]^+$ (100%); 473, $[Tb(hfa)(HCOCHCOH)(F)_2]^+$ (8%); 385, $[Tb(hfa)(F)]^+$ (41%); 335, $[Tb(CF_3COCHCO)(F)_2]^+$ (90%).

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)

	x	y	z	U(eq)[a]
Tb(1)	1635(1)	2143(1)	1033(1)	43(1)
O(1)	1326(8)	225(7)	514(5)	58(3)
C(1)	5403(7)	4471(7)	2037(5)	112(11)
F(1)	6449(9)	4479(10)	1897(7)	99(4)
F(2)	5061(12)	5373(8)	1953(9)	188(9)
F(3)	5489(11)	4379(10)	2776(6)	109(5)
F(1′)	6019(16)	4989(13)	1653(8)	70(7)
F(2′)	6130(15)	4109(11)	2570(10)	167(21)
F(3′)	4848(12)	5125(13)	2411(12)	84(9)
C(2)	4445(10)	3488(11)	1409(7)	57(5)
O(2)	3639(7)	3101(7)	1720(4)	50(3)
O(3)	2141(7)	1439(7)	2226(5)	54(3)
C(3)	4503(12)	3196(11)	640(7)	60(5)
C(4)	3736(9)	2334(9)	61(7)	59(6)
O(4)	2785(8)	1793(7)	131(5)	61(4)
C(5)	4009(7)	1918(7)	−771(4)	89(8)
F(4)	4674(11)	2676(10)	−923(6)	210(10)
F(5)	4551(11)	1131(11)	−733(7)	181(9)
F(6)	3028(9)	1602(9)	−1341(4)	137(7)
C(6)	2122(8)	5248(7)	37(5)	96(9)
F(7)	1286(12)	5816(9)	19(10)	119(6)
F(8)	2975(12)	5631(10)	709(8)	123(6)
F(9)	2551(14)	5296(10)	−575(8)	106(5)
F(7′)	2013(19)	5860(9)	691(9)	94(7)
F(8′)	3255(11)	5339(10)	74(14)	115(9)
F(9′)	1562(17)	5544(11)	−594(9)	130(10)
C(7)	1566(11)	4031(11)	−23(7)	62(6)
O(7)	1766(8)	3783(7)	659(5)	59(4)
C(8)	930(14)	3398(11)	−766(8)	72(6)
C(9)	320(11)	2361(11)	−865(8)	64(6)
O(9)	322(7)	1840(7)	−323(5)	60(4)
C(10)	−537(7)	1722(7)	−1729(4)	127(13)
F(10)	−181(11)	2087(10)	−2292(5)	77(4)
F(11)	−512(15)	701(9)	−1834(7)	119(6)
F(12)	−1631(9)	1859(14)	−1773(8)	175(11)
F(10′)	−7(14)	1009(14)	−2064(8)	165(15)
F(11′)	−1536(12)	1235(16)	−1651(8)	96(7)
F(12′)	−764(17)	2390(11)	−2187(7)	101(8)
C(11)	715(7)	4969(7)	2740(5)	89(8)
F(13)	1540(10)	5033(9)	3382(6)	173(8)
F(14)	1079(13)	5624(7)	2356(8)	186(11)
F(15)	−209(10)	5215(9)	2928(7)	172(8)
C(12)	390(10)	3773(11)	2184(7)	57(6)
O(12)	1347(8)	3424(7)	2111(5)	59(4)
C(13)	−749(13)	3273(13)	1818(9)	70(7)
C(14)	−1070(13)	2216(10)	1289(9)	67(6)
O(14)	−358(7)	1681(7)	1083(5)	58(4)
C(15)	−2419(8)	1650(8)	944(6)	182(21)
F(16)	−2514(11)	608(10)	795(12)	126(7)
F(17)	−2999(11)	1960(14)	1470(10)	123(6)
F(18)	−2883(13)	1922(17)	269(10)	211(13)
F(16′)	−2652(13)	1204(20)	171(9)	184(17)
F(17′)	−3097(10)	2356(12)	1050(14)	89(7)
F(18′)	−2637(12)	906(16)	1329(14)	151(13)
Tb(2)	4184(1)	2974(1)	4651(1)	41(1)
C(16)	7196(7)	1084(7)	5549(5)	90(9)
F(19)	6724(11)	499(12)	5958(8)	116(6)
F(20)	7877(11)	566(12)	5198(7)	99(5)
F(21)	7842(11)	1981(10)	6039(8)	104(5)
F(19′)	7099(16)	45(9)	5431(11)	109(8)
F(20′)	8237(9)	1509(18)	5495(12)	142(11)
F(21′)	7098(16)	1478(18)	6267(6)	117(9)
C(17)	6169(11)	1341(9)	4886(8)	58(6)
O(17)	5494(8)	1911(7)	5167(5)	63(4)
C(18)	6053(13)	930(11)	4072(8)	67(6)
C(19)	5159(10)	1104(9)	3473(8)	57(5)
O(19)	4349(8)	1642(7)	3530(5)	55(3)
C(20)	5033(7)	516(7)	2569(5)	88(9)
F(22)	6100(10)	375(12)	2495(6)	93(5)
F(23)	4304(14)	−433(10)	2379(7)	156(9)
F(24)	4592(14)	1102(11)	2077(6)	106(5)
F(22′)	3901(11)	41(16)	2203(7)	101(8)
F(23′)	5370(19)	1232(10)	2184(7)	126(10)
F(24′)	5718(16)	−211(13)	2560(7)	94(7)
O(20)	5430(8)	3983(7)	5977(5)	61(4)
O(21)	3272(8)	4430(8)	4974(5)	63(4)
C(21)	2250(8)	2113(7)	6558(5)	99(9)
F(25)	2641(16)	1272(12)	6740(8)	125(7)
F(26)	2919(14)	2984(11)	7071(6)	128(7)
F(27)	1144(10)	2047(14)	6591(7)	119(6)
F(25′)	3317(12)	2102(18)	7001(8)	111(8)
F(26′)	1890(19)	2964(12)	6876(8)	100(8)
F(27′)	1505(16)	1251(12)	6530(8)	101(7)
C(22)	2300(11)	2150(9)	5678(8)	64(6)
O(22)	3369(9)	2376(8)	5617(5)	65(4)
O(23)	3572(7)	3700(6)	3420(4)	48(3)
C(23)	1254(11)	1916(12)	5065(9)	64(6)
C(24)	1266(11)	1909(9)	4275(7)	53(5)
O(24)	2146(7)	2126(7)	4006(5)	52(3)
C(25)	−12(7)	1643(8)	3608(5)	114(10)
F(28)	−136(12)	2447(13)	3279(10)	228(15)
F(29)	−73(11)	792(13)	3054(8)	182(11)
F(30)	−862(8)	1471(13)	3945(7)	86(4)
F(28′)	125(10)	1403(14)	2889(6)	55(4)
F(29′)	−695(10)	836(13)	3715(9)	106(8)
F(30′)	−514(12)	2475(13)	3684(10)	128(11)
O(26)	5928(8)	3861(8)	4436(5)	65(4)
C(26)	6732(10)	4635(9)	4663(6)	41(4)
C(27)	7936(7)	4432(7)	4459(5)	99(9)
F(31)	8604(11)	5339(10)	4507(11)	163(9)
F(32)	8503(11)	3948(13)	4972(8)	111(5)
F(33)	7683(10)	3822(12)	3732(7)	95(5)
F(31′)	7970(13)	4719(19)	3795(9)	118(9)
F(32′)	8846(9)	5007(16)	5046(9)	84(6)
F(33′)	7983(14)	3424(10)	4369(14)	197(18)
O(100)	4004(27)	7065(26)	2772(18)	136(10)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

X-ray Crystal Structure of 1. A single crystal of complex **1** was obtained as outlined in the above part of the Experimental Section. The crystal used measured $0.37 \times 0.40 \times 0.47$ mm and was mounted onto a glass fiber with epoxy resin and coated with epoxy to reduce any possible crystal decomposition during data collection. The accurate unit cell parameters for **1** were obtained by means of least-squares analysis of 20 centered reflections. Data for compound **1** were collected on a Siemens P4/PC diffractometer using graphite-monochromated Mo Kα radiation. A summary of the crystal data, data collection, and refinement parameters is given in Table 1. Two standard reflections were monitored every 50 reflections and showed no significant variation over the data collection. A total of 8525 reflections were measured of which 6506 were observed [$F > 4.0\sigma(F)$]. The structure of **1** was solved by the heavy-atom method and refined by full-matrix least squares with absorption-corrected data and using anisotropic thermal parameters for non-hydrogen atoms.[13] All but two of the eleven unique CF_3 groups were found to be disordered. The estimated occupancies of the two principal orientations were 0.60 and 0.40. The full occupancy F atoms were refined anisotropically, and the partial occupancy atoms isotropically. The geometries of all the CF_3 groups were optimized and each refined subject to an individual refined C–F distance constraint. The hydrogen atom positions were calculated, assigned fixed isotropic U values, and allowed to ride on their parent carbon atoms. The positions of the hydroxyl and water protons were not located. Final atomic parameters are given in Table 2, and selected bond lengths and angles in Tables 3 and 4.

Table 3. Selected Bond Lengths (Å) for Complex **1**

Tb(1)–O(1)	2.392(8)	Tb(1)–O(2)	2.373(7)
Tb(1)–O(3)	2.403(9)	Tb(1)–O(4)	2.321(10)
Tb(1)–O(7)	2.321(9)	Tb(1)–O(9)	2.401(8)
Tb(1)–O(12)	2.363(9)	Tb(1)–O(14)	2.342(9)
Tb(2)–O(17)	2.323(10)	Tb(2)–O(19)	2.392(8)
Tb(2)–O(20)	2.399(7)	Tb(2)–O(21)	2.318(10)
Tb(2)–O(22)	2.328(10)	Tb(2)–O(23)	2.490(8)
Tb(2)–O(24)	2.358(7)	Tb(2)–O(26)	2.336(10)

Results and Discussion

The well-known and often used synthetic strategy for the preparation of complex **1**, using a mixed H_2O–MeOH solvent

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(13) SHELXTL version 4.2, Siemens X-ray Analytical Instruments, 1991.

Table 4. Selected Bond Angles (deg) for Complex 1

O(1)–Tb(1)–O(2)	117.9(3)	O(1)–Tb(1)–O(3)	75.3(3)
O(2)–Tb(1)–O(3)	77.0(3)	O(1)–Tb(1)–O(4)	71.1(3)
O(2)–Tb(1)–O(4)	73.0(3)	O(3)–Tb(1)–O(4)	115.7(3)
O(1)–Tb(1)–O(7)	143.4(3)	O(2)–Tb(1)–O(7)	74.8(3)
O(3)–Tb(1)–O(7)	140.3(3)	O(4)–Tb(1)–O(7)	81.8(3)
O(1)–Tb(1)–O(9)	76.7(3)	O(2)–Tb(1)–O(9)	134.7(3)
O(3)–Tb(1)–O(9)	145.6(3)	O(4)–Tb(1)–O(9)	72.5(3)
O(7)–Tb(1)–O(9)	71.9(3)	O(1)–Tb(1)–O(12)	140.5(3)
O(2)–Tb(1)–O(12)	77.9(3)	O(3)–Tb(1)–O(12)	73.7(3)
O(4)–Tb(1)–O(12)	145.8(3)	O(7)–Tb(1)–O(12)	73.5(3)
O(9)–Tb(1)–O(12)	119.6(3)	O(1)–Tb(1)–O(14)	81.6(3)
O(2)–Tb(1)–O(14)	147.7(3)	O(3)–Tb(1)–O(14)	84.5(3)
O(4)–Tb(1)–O(14)	139.2(3)	O(7)–Tb(1)–O(14)	105.5(3)
O(9)–Tb(1)–O(14)	72.0(3)	O(12)–Tb(1)–O(14)	71.6(3)
O(17)–Tb(2)–O(19)	71.7(3)	O(17)–Tb(2)–O(20)	71.9(3)
O(19)–Tb(2)–O(20)	137.9(3)	O(17)–Tb(2)–O(21)	145.3(3)
O(19)–Tb(2)–O(21)	143.0(3)	O(20)–Tb(2)–O(21)	75.5(3)
O(17)–Tb(2)–O(22)	76.5(4)	O(19)–Tb(2)–O(22)	118.1(3)
O(20)–Tb(2)–O(22)	72.3(3)	O(21)–Tb(2)–O(22)	82.7(4)
O(17)–Tb(2)–O(23)	139.6(3)	O(19)–Tb(2)–O(23)	73.9(3)
O(20)–Tb(2)–O(23)	126.4(3)	O(21)–Tb(2)–O(23)	71.3(3)
O(22)–Tb(2)–O(23)	140.0(3)	O(17)–Tb(2)–O(24)	117.5(3)
O(19)–Tb(2)–O(24)	78.0(3)	O(20)–Tb(2)–O(24)	138.8(3)
O(21)–Tb(2)–O(24)	80.7(3)	O(22)–Tb(2)–O(24)	71.8(3)
O(23)–Tb(2)–O(24)	74.4(3)	O(17)–Tb(2)–O(26)	82.2(3)
O(19)–Tb(2)–O(26)	80.4(3)	O(20)–Tb(2)–O(26)	74.4(3)
O(21)–Tb(2)–O(26)	100.3(4)	O(22)–Tb(2)–O(26)	144.5(3)
O(23)–Tb(2)–O(26)	71.7(3)	O(24)–Tb(2)–O(26)	143.7(3)
Tb(2)–O(21)–C(26A)	153.8(8)	Tb(2)–O(26)–C(26)	146.6(9)
O(26)–C(26)–O(21A)	128.3(12)		

with $TbCl_3$ and sodium hexafluoroacetylacetone, was expected to yield $Tb(hfa)_3(H_2O)$ (as shown in eq 1).[14] However, we obtained a rather different product on workup compared to that of Sievers et al. (see eq 2).

$$TbCl_3(H_2O)_6 + 3Na(hfa) \xrightarrow{H_2O/MeOH} Tb(hfa)_3(H_2O) + 3NaCl \quad (1)$$

$$4TbCl_3(H_2O) + 12Na(hfa) \xrightarrow{H_2O/MeOH} [Tb_2(hfa)_4(OAc_F)_2(H_2O)_4][Tb(hfa)_3(H_2O)_2]_2 + 12NaCl \quad (2)$$

The product obtained is soluble in benzene, toluene, and also *n*-hexane. This complex also exhibits good stability in the atmosphere over a long time scale. The infrared spectra of complex 1 as either Nujol or hexachlorobutadiene mulls reveal the presence of several broad overlapping peaks. The presence of either CF_3COO^- or hfa ligands coordinated to the metal center cannot, in this particular instance, be definitely assigned although peaks attributable to these ligands are observed in the range 1500–1650 cm^{-1}. However, a broad peak for the hydrogen-bonded water molecules is observed at 3451 cm^{-1}.

Mass spectrometric studies have been reported previously for a wide range of homoleptic and Lewis base stabilized lanthanide β-diketones. In the gas phase such materials have been shown to consist of $[ML_3]^+$, $[M_2L_5]^+$, and $[M_2L_6]^+$ ions.[15] For complex 1, the highest mass peak was observed at 780 amu for $[Tb(hfa)_3]^+$, and below this lower mass fragments $[Tb(hfa)_2(CF_3COCHCO)]^+$ at 711 and $[Tb(hfa)_2]^+$ at 573 amu were observed. Clearly, this mass spectrometric data implies that complex 1 dissociates in the vapor phase with the $Tb(hfa)_3$ fragment from the $Tb(hfa)_3(H_2O)_2$ unit being reasonably volatile; in contrast the dimeric $[Tb_2(hfa)_4(CF_3COO)_2]$ component of compound 1 is evidently involatile under these conditions.

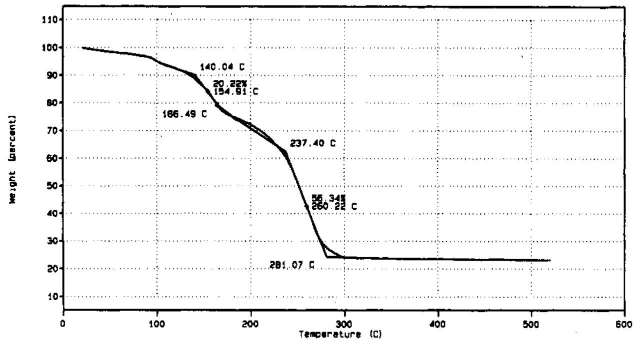

Figure 1. Thermogravimetric analysis plot for compound 1.

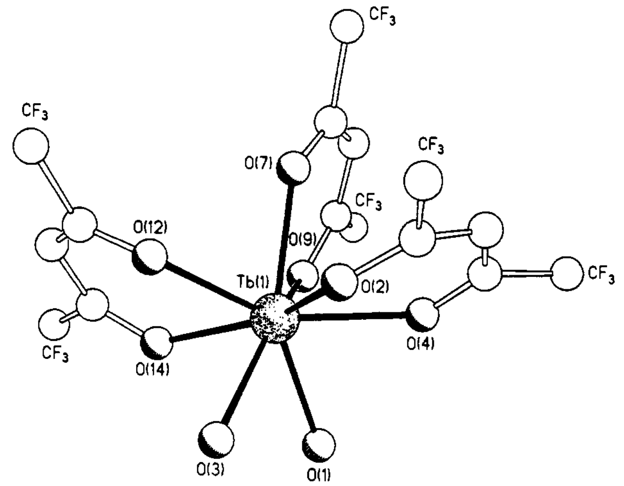

Figure 2. Molecular structure of the monomeric component of 1, showing the atom-numbering scheme, with the fluorine atoms being omitted for clarity.

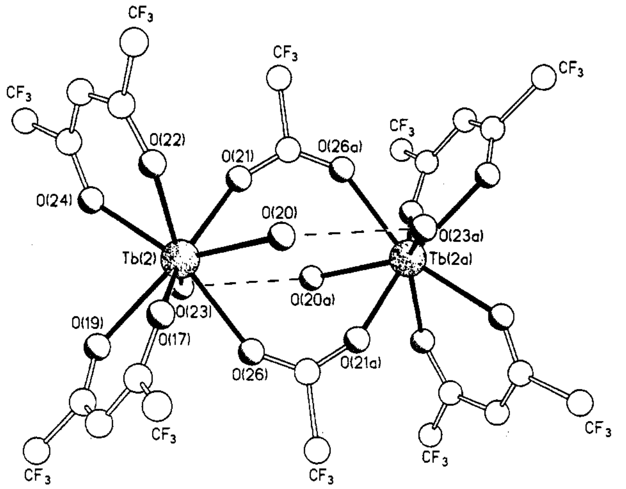

Figure 3. Molecular structure of the dimeric unit of 1, showing the atom-numbering scheme, with the fluorine atoms being omitted for clarity.

Thermal Behavior. The DSC and TGA spectra for this complex have three broad isothermal processes, occurring in a continuous manner over the temperature range 90–300 °C. The differential scanning calorimetry plot of complex 1 reveals a broad endotherm centered at 99 °C (–2.21 mcal/mg), which is mirrored in the thermogravimetric curve (see Figure 1) with a 6% weight loss (calculated for loss of nine water molecules is 5.8%). A second major exothermic process is observed in the DSC centered at 142 °C (–25 mcal/mg); this process is coupled with a simultaneous 20% weight loss in the TGA in the temperature range 120–175 °C and is attributed to the loss of all the CF_3COO and several hfa ligands (calc for $2CF_3COO$ and 2hfa, 21%). Finally, a third endotherm is observed in the DSC at 265 °C (–9 mcal/mg),

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[14] Eisentraut, K. J.; Sievers, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 5254.
[15] See for example: (a) Risby, T. H.; Jurs, P. C.; Lampe, F. W.; Yergey, A. L. *Anal. Chem.* **1974**, *46*, 161. (b) McDonald, J. D.; Margrave, J. L. *J. Less-Common Met.* **1968**, *14*, 236.

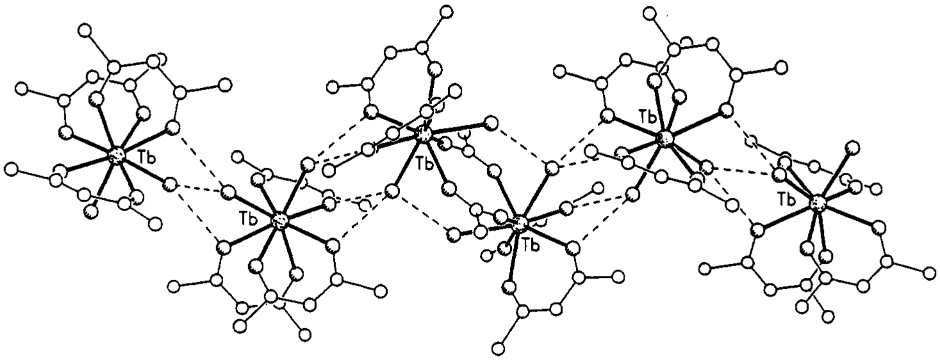

Figure 4. Part of the continuous chain of H-bonded linked monomers and dimers in the crystal structure of **1**. The fluorine atoms are omitted for clarity.

which correlates with a final weight loss of 56% (calc for 8hfa, 54%) in the TGA (190–270 °C), with elimination of the remaining hfa ligands to yield a residue (24%). This material is most likely to contain fluoride, and a possible suggestion is TbO_nF_m (25.1%). If the TGA had been run under O_2/O_2-saturated water vapor, then a pure Tb_2O_3 phase may have been obtained.

As the precise nature of compound **1** could not be completely elucidated by spectroscopic methods, a single-crystal X-ray structural study was undertaken to unambiguously identify the structural composition of the complex.

X-ray Structure of {[$Tb_2(hfa)_4(O_2CCF_3)_2(H_2O)_4$][$Tb(hfa)_3(H_2O)_2$]$_2$·$H_2O$}. The X-ray structure data for compound **1** shows the unit cell to contain two monomeric units and one dimeric unit positioned about a center of symmetry and two partial occupancy water molecules. Each monomeric terbium unit is eight coordinate (see Figure 2) and comprises three chelating hfa ligands and two water molecules arranged in a distorted square antiprismatic geometry. The Tb–O distances are in the range 2.321(9)–2.403(9) Å.

The dimeric unit (illustrated in Figure 3) consists of two terbium metal centers; each of these is coordinated to two hfa ligands and two water molecules, and they are bridged by two trifluoroacetate molecules. The geometry at the terbium centers in this dimer is also found to be distorted antiprismatic, and the Tb–O distances are in the range 2.318(10)–2.490(8) Å. The CF_3COO bridging ligands have noticeably enlarged O–C–O bond angles of 128.3(12)°. The Tb–O distances involving the water ligands [2.45(9) Å] are significantly longer than those to the hfa ligands [2.35(9) Å]. There is no apparent differentiation between the Tb–O(CF_3COO) and Tb–O(hfa) distances. The Tb–O(hfa) values in both the monomeric and dimeric components of **1** are similar to those reported for other related lanthanide β-diketonates. An extensive review of the literature did not yield any terbium-based diketonates or alkoxides for comparison.[12,16] Within each dimer there are, in addition to the trifluoroacetate bridging ligands, pairs of intramolecular hydrogen bonding O–H–O bridges, between the water molecules on the two terbium metal centers [2.92(1) Å].[17]

In the crystal lattice (see Figure 4), the monomers and dimers are further linked via intermolecular O–H–O hydrogen bonds, between water molecules and the carbonyl oxygen atoms of the hfa ligands, to form chains that have the sequence ...M, M, D, M, M, D, M, M, D, M, M... (where M = monomer and D = dimer). Within these chains, the monomer–dimer Tb(1)–Tb(2) distances are 6.10 Å, the intradimer Tb(2)–Tb(2a) distance is 5.07 Å, and the Tb(1)–Tb(1c) distances are ca. 6 Å. The intermolecular hydrogen bonding appears to be weaker (>3 Å) than the intramolecular (2.92 Å), but it is still strong enough to form one-dimensional chains. A similar combination of both intra- and intermolecular hydrogen bonding has been recently reported for the compound $Y_2(\mu\text{-}OAc)_2(acac)_4(H_2O)_2$, which forms extended chains in the *b* axis.[18]

The origin of the trifluoroacetate molecules is an intriguing one, and one that previous researchers have studied. It had been previously suggested that hexafluoroacetylacetone reacts with water to form initially a "dihydrate", i.e. [hfa-H·$2H_2O$];[19] however, more recent rigorous studies by Christou et al.[20] have demonstrated that this reaction is far from simple. These latter researchers have demonstrated that hfa-H reacts with water to yield [$F_3CC(OH)_2CH_2C(OH)_2CF_3$], while further reaction produces trifluoroacetic acid and $F_3CCOCH_2COCH_3$. Therefore, this reaction is essentially the reverse of a Claissen condensation, and ultimately the pH of the reaction solution must have a profound effect on the nature of the product and how the hfa ligand is cleaved. Indeed, this reaction is presumably driven by the presence of a small amount of unreacted sodium hydroxide (in the water–methanol mixed solvent) and then stabilized by the basic media. Our observations are in good agreement with those of other researchers on a related yttrium β-diketone complex.[18]

Conclusions

This is an unexpected and unusual complex, incorporating both monomeric and dimeric Terbium-centered molecular units that are linked via intra- and intermolecular hydrogen bonding. The complex appears to have been formed by serendipity under relatively simple reaction conditions where one would expect just a simple monomeric unit to be formed. The formation of the trifluoroacetate ligands is interesting and warrants further study and expansion to other β-diketones, especially since such acac-based ligands have found extensive application as sol–gel based modifiers.

Acknowledgment. We thank the SERC for a studentship (D.J.O.) and for the X-ray diffractometers, the CASE sponsor Inorgtech (Dr. Tim Leedham) for the simultaneous thermal analysis equipment, and the Royal Society (for an inert-atmosphere glovebox). We also thank Professor D. M. P. Mingos and Dr. G. B. Young for their invaluable help and assistance.

Supplementary Material Available: Tables giving crystal data and details of the structure determination, complete bond lengths and angles, fractional atomic coordinates and isotropic thermal parameters for the hydrogen atoms, and anisotropic thermal parameters for complex **1** and a differential scanning calorimetry plot (8 pages). Ordering information is given on any current masthead page.

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(16) A comprehensive search of the Cambridge Crystallographic Data base revealed that no relevant terbium structures were available for comparison.

(17) The H-atoms in these bridges have not been located, and the assumption of the presence of H-bonds is based on the O–O internuclear distances, which are 2.94 Å.

(18) Poncelet, O.; Hubert-Pfalzgraf, L. G. *Polyhedron* **1990**, *9*, 1305.

(19) Richardson, M. F.; Wagner, W. F.; Sands, D. E. *J. Inorg. Nucl. Chem.* **1968**, *30*, 1275.

(20) Bouwman, E.; Huffman, J. C.; Lobkovsky, E. B.; Christou, G.; Tsai, H.-L.; Hendrickson, D. N. *Inorg. Chem.* **1992**, *31*, 4436.