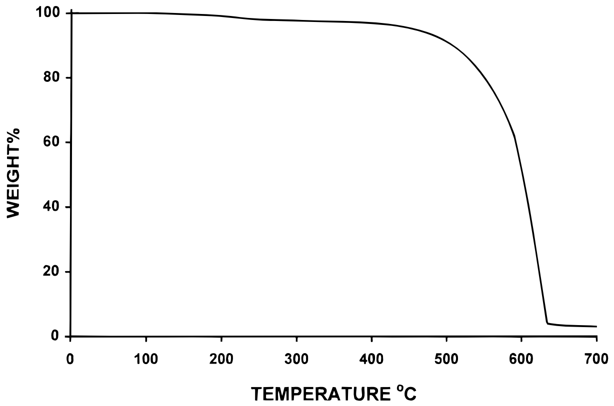

Figure 2. TGA analysis of complex **1**, carried out under an argon atmosphere (15 sccm, 10 °C/min).

the chelating ring. A similar trend has been observed for other non-lanthanide β-ketoiminate complexes.[6,7]

Compound **1** is volatile and thermally stable in both the vapor and condensed phases, up to the sublimation temperature. The solid−vapor transition appears to be a single-step event (Figure 2), which remarkably occurs at 600 °C (1 atm). This portrayal of thermal robustness is unique among Ln−N interactions, which generally are unstable at such elevated temperature. To our knowledge, no other molecular lanthanide compound displays this degree of thermal stability. The great thermal robustness of **1** may be comparable to that shown previously by metal complexes with intramolecular coordination of Lewis base bearing pendant arms on anionic ligands.[15]

The magnetic susceptibility of **1** was measured, and diamagnetic corrections were calculated using Pascal's constants. A plot of μ_{eff} vs T (Supporting Information) shows nearly temperature-independent behavior, decreasing gradually from $\mu_{\mathrm{eff}} = 4.41\ \mu_{\mathrm{B}}$ at 295 K to $\mu_{\mathrm{eff}} = 3.51\ \mu_{\mathrm{B}}$ at 5.17 K. The value at 295 K is comparable to the 4.5 μ_{B} predicted by Van Vleck. Deviation from anticipated behavior in rare earth compounds is not unusual and may arise in part from the effects of a weak crystal field in the ground state.[16]

Summary

A new β-ketoiminate ligand platform was prepared and employed in the formation of a lanthanide compound, which possesses unprecedented thermal stability. Additionally, it has reduced oxidative sensitivity compared to other lanthanide examples, being able to be handled in the open atmosphere for brief exposures without any measurable decomposition. The magnetic characterization is consistent with that proposed for an f^{13} example. The pseudooctahedral metal center portrays a meridinal N_3 and O_3 ligand arrangement between the defined planes. Perhaps the most remarkable feature of this first example of a new class of compounds is the extreme thermal robustness that is displayed. This is in marked contrast to reported barium bis(β-ketoiminate) examples,[7] and the origin of this unexpected stability currently is undergoing further exploration.

Experimental Section

General Comments. Manipulations were performed under a dried Ar atmosphere, employing standard Schlenk techniques, or in an inert gas-filled glovebox. The solvents were degassed and freshly distilled from sodium or potassium/benzophenone prior to use. Handling and mounting of crystals on the diffractometer were carried out in a 77 K Ar stream.[17]

Physical Measurements. See Supporting Information for Physical Measurements and X-ray Measurements details.

Preparation of 5-*N*-(*n*-Pr)-2,2,6,6-tetramethyl-3-heptanone (2). Under an argon atmosphere, 34.4 g (134 mmol) of 2,2,6,6-tetramethyl-5-(trimethylsiloxy)hept-4-en-3-one[18] and 8.26 g (140 mmol) of *n*-Pr amine were heated in a Schlenk flask with vigorous stirring for 3 h at 46−48 °C. The reaction mixture was distilled to afford 11.76 g (39% yield) of 5-*N*-(*n*-Pr)-2,2,6,6-tetramethyl-3-heptanone as a colorless liquid; bp = 267 °C/760 Torr. ^{1}H NMR [300 MHz, C_6D_6, δ, ppm]: 0.79 (t, 3H, CH_3), 1.05 (s, 9H, (CH_3)$_3$-CCN), 1.31 (s, 9H, (CH_3)$_3$CCO), 1.33 (m, 2H, CH_2), 2.99 (m, 2H, NCH_2), 5.47 (s, 1H, CH), 12.30 (br s, 1H, NH). ^{13}C NMR [300 MHz, C_6D_6, δ, ppm]: 11.26 (s, CH$_3$CH$_2$), 23.89 (s, CH$_3$$CH_2$), 28.35 (s, NC($CH_3$)$_3$), 28.96 (s, COC($CH_3$)$_3$), 35.80 (s, N$C$(CH$_3$)$_3$), 41.81 (s, O$C$(CH$_3$)$_3$), 47.03 (s, N$CH_2$), 85.95 (s, CH), 173.18 (s, CN), 203.10 (s, CO). ^{14}N NMR [400 MHz, C_6D_6, δ, ppm]: 269.99. IR [cm^{-1}]: 1612, 2365. MS (EI, 70 eV): 225, 210, 182, 168, 57. Anal. Calcd for $C_{14}H_{27}NO$: C, 74.61; H, 12.08. Found: C, 74.55; H, 12.64.

Preparation of Yb Tris(β-ketoiminate) (1). Under an Ar atmosphere 2.80 g (12.45 mmol) of **2** was dissolved in 50 mL of Et_2O and added dropwise to a suspension of 0.49 g (12.45 mmol) of KH in 50 mL of Et_2O. During the addition the KH slowly disappeared and the reaction mixture became transparent. This solution was added to a suspension of 1.16 g (4.15 mmol) of anhydrous $YbCl_3$ in 50 mL of Et_2O at ambient temperature. After the solution was stirred overnight, the solvent was removed, the product was extracted with hexane, and after filtration, the obtained yellow solution was evaporated. The residue was redissolved in 20 mL of toluene and the volume gradually reduced until precipitation set in. X-ray-suitable, air-stable yellow crystals were grown from toluene solution at ambient temperature. Prior to mounting in the X-ray beam, the yellow solid was washed with a small amount of cold toluene. Yield, 2.63 g (75%); mp = 120 °C. Sublimation conditions: 160−170 °C/10^{-4} Torr. MS (EI, 70 eV, m/z, 185 °C): 846 [M$^+$], 789, 623, 523, 398, 366, 297 168. IR [Nujol, cm^{-1}]: 2940, 2867, 1570, 1556, 1481, 1419, 1348, 1270, 1222, 1156, 1108, 1054, 1028, 914, 879, 843, 817, 787, 707, 620, 593, 511, 491, 453, 411. Anal. Calcd for $C_{42}H_{78}$-$Yb_1N_3O_3$: C, 59.61; H, 9.29. Found: C, 59.24; H, 9.46.

Acknowledgment. DARPA's financial support and Dr. Z. J. Zhang's aid with magnetic measurements are appreciated. W.S.R. was the recipient of an Alexander von Humboldt Award during 1998−1999 with Professor Dr. H. Schumann at the Technische Universität Berlin.

Supporting Information Available: Listings of atomic coordinates, anisotropic displacement parameters, full interatomic angles and bond distances, physical measurements, and a plot of μ_{eff} vs T. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Single-crystal X-ray analysis of **1** was performed utilizing a Siemens SMART CCD diffractometer at 173 K. Crystal data: $Yb_1N_3O_3C_{42}H_{78}$, $M_r = 846.11$ g mol^{-1}, irregularly shaped yellow, transparent crystal, dimensions 0.25 mm × 0.30 mm × 0.35 mm, triclinic, space group $P\bar{1}$, $a = 10.4591(2)$ Å, $b = 12.8775(3)$ Å, $c = 18.3311(3)$ Å, $\alpha = 100.5610(10)°$, $\beta = 92.6470(10)°$, $\chi = 110.48°$; $V = 2257.42(8)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.245$ g cm^{-3}, $\mu = 2.108$ mm^{-1}, $F(000) = 890$, $1.14 < \phi < 23.23°$, $-11 < h < 11$, $-7 < k < 14$, $-20 < l < 20$, R1 = 0.0182, wR2 = 0.0502, GOF = 1.106 for 488 parameters, largest diffr peak and hole = 0.708 and −0.497 e Å^{-3}.

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