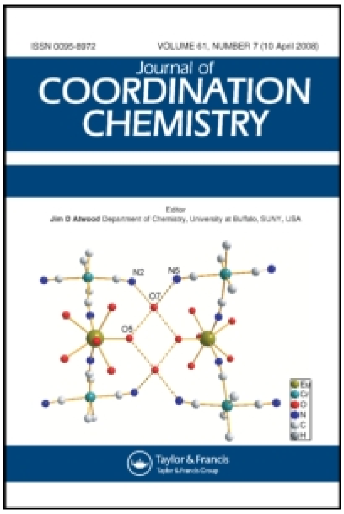

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Physical and Structural Characterization of Ce(IV) β-Diketonate Complexes: Evidence for Geometrical Isomers in the Solid-State

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PHYSICAL AND STRUCTURAL CHARACTERIZATION OF Ce(IV) β-DIKETONATE COMPLEXES: EVIDENCE FOR GEOMETRICAL ISOMERS IN THE SOLID-STATE

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The Ce(IV) β-diketonate complexes CeL_4 [where L is txhd (2,2,6-trimethyl-3,5-heptanedionate) **1**; tmod (2,2,7-trimethyl-3,5-octanedionate) **2**; tmhd (2,2,6,6-tetramethyl-3,5-heptanedionate) **3**] were prepared by the interaction of the sodium salt of the diketonate with cerium(III) nitrate hexahydrate in aqueous ethanol solution. Differential scanning calorimetry and thermogravimetric analysis showed that **1** has a significantly lower sublimation temperature, but higher decomposition temperature than **3**. The solid-state structures of the three complexes were determined *via* single crystal x-ray diffraction methods. Complex **2**, which does not sublime, had significantly closer intermolecular contacts than those found for **1** and **3**.

Keywords: Cerium(IV) complexes; β-diketonate ligands; Volatile metal complexes; Chemical vapor deposition; Crystal structures

INTRODUCTION

The identification of volatile cerium complexes as potential precursors for metal-organic chemical vapor deposition (MOCVD) processes has been an area of ongoing research. As a dopant in SrS and $CaGa_2S_4$, cerium can produce blue-green and blue electroluminescent (EL) phosphors, respectively. $Ce(tmhd)_4$ (tmhdH = 2,2,6,6-tetramethyl-3,5-heptanedione) can serve as the cerium source of doping SrS by atomic layer epitaxy (ALE) [1] or for doping SrS [2,3] and $CaGa_2S_4$ *via* MOCVD methods [4–6]. $Ce(tmhd)_4$ has also found utility as an MOCVD [7,8] and ALE [9] precursor for the deposition of cerium dioxide, a potential buffer layer for the growth of $YBa_2Cu_3O_{7\text{-}x}$ high-T_c superconducting films [10], among others [11].

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The thermal and CVD properties of other homoleptic Ce(IV) β-diketonate complexes, containing ligands such as 6,6,6-trifluoro-2,2-dimethyl-3,5-hexanedionate [12,13] and 1-phenyl-5-methyl-1,3-hexanedionate [14] have been evaluated, as well. Heteroleptic Ce(III) β-diketonates [11–13,15], along with air-sensitive tris[*bis* (trimethylsilyl)amide]cerium(III), have also been evaluated as precursors for MOCVD or ALE processes [16].

In general, metal β-diketonate complexes are air-stable, have high vapor pressures, sublime with minimal decomposition, and can be reduced at relatively low temperatures. Our goal was to expand the pool of possible Ce β-diketonate MOCVD precursors, so that a range of deposition temperatures and precursor volatilities was available. Attenuation of these thermal parameters would facilitate the fabrication of compounds, such as SrS : Ce, using a liquid delivery system in which a "cocktail" of appropriate precursors are dissolved in a common solvent and injected into a vaporizer prior to introduction in the MOCVD reaction chamber.

The useful vaporization and MOCVD properties of $Ce(tmhd)_4$ are, in part, a consequence of the bulky, peripheral *tert*-butyl substituents of the ligands. However, we have found in related studies involving Cu(II) complexes, that unsymmetrical ligands derived from $Me_3CC(O)CH_2C(O)R$ (R = a hydrocarbyl moiety other than *tert*-butyl) often result in greater volatility and lower melting points in contrast to the tmhd analog ($R = CMe_3$) [17]. We chose for our initial Ce(IV) studies, $Me_3CC(O)CH_2C(O)CHMe_2$ (2,2,6-trimethyl-3,5-heptanedione; txdhH) and $Me_3CC(O)CH_2C(O)CH_2CHMe_2$ (2,2,7-trimethyl-3,5-octanedione; tmodH), which have peripheral *iso*-propyl and *iso*-butyl substituents, respectively, and where the steric demand has been modulated. Herein, we report on the thermal properties an crystal structures of $Ce(txhd)_4$ (**1**) and $Ce(tmod)_4$ (**2**) in order to make comparisons to $Ce(tmhd)_4$ (**3**), the structure of which we have also determined under comparable conditions.

EXPERIMENTAL

Materials and Methods

Cerium(III) nitrate hexahydrate was purchased from Strem Chemicals. The ligands tmodH and tmhdH were purchased form Gelest Chemicals and Lancaster Chemicals, respectively, and used without further purification.

Melting points were measured using a TA Instruments DSC 2920 Differential Scanning Calorimeter (DSC) with samples (~ 1.3 mg) in hermetically sealed aluminum pans. DSC measurements were obtained at a heating rate of 10°C/min up to 500°C and referenced relative to indium. Thermogravimetric analysis (TGA) was performed using a TA Instruments TGA 2050 Thermogravimetric Analyzer on ~ 1.5 mg of sample. Heating rates were 1°C/min to 35°C and 5°C/min from 350–600°C under a nitrogen purge ($100\,cm^3$/min).

Preparation of 2,2,6-Trimethyl-3,5-Heptanedione (txhdH)

This dione was synthesized *via* a modification of the literature method [18]. Pinacolone (5.0 g, 50 mmol) and ethyl isobutyrate (5.8 g, 50 mmol) were added dropwise simultaneously to sodium hydride (1.2 g, 50 mmol) in dimethoxyethane (120 mL) over a 30 min period. The reaction mixture was then heated under reflux for 1 h, after which 6 M HCl (25 mL) was carefully added, followed by water (75 mL) to improve separation of the liquid phases. The organic layer was separated from the aqueous phase, which was extracted with hexane (3 × 75 mL). The organic layers were combined and the solvent removed on a rotary evaporator. Fractional distillation of the residue at atmospheric pressure (material collected between 145 and 210°C) provided txhdH of sufficient purity for subsequent reaction. The unoptimized yield was 2.32 g (28%).

Preparation of Ce(IV) β-Diketonate Complexes

The Ce(IV) complexes were prepared *via* the following general procedure. The appropriate β-diketonate (50 mmol) was dissolved in absolute ethanol (20 mL) and NaOH (2.0 g, 50 mmol) was dissolved in 1 : 1 ethanol/water (40 mL). The NaOH solution was slowly added to the solution of β-diketonate with stirring. After the addition was complete, stirring was continued for 15 min.

A solution of cerium(III) nitrate hexahydrate (12 mmol, 5.2 g) in water (20 mL) was added dropwise with stirring to the freshly prepared solution of the sodium β-diketonate. After the addition was complete, the volume of the reaction mixture was reduced by half under vacuum, followed by the addition of water (10 mL) and continued evacuation for 1 h. The product was filtered and rinsed with water (100 mL). Air was pulled over the product on the filter for 1 h, followed by further drying *in vacuo*. Yields of crude product ranged from 60–90%. The volatile products **1** and **3** were further purified by sublimation at ~ 120°C, 0.1 mm Hg and used for the DSC and TGA experiments. Melting points for the complexes were: **1**, 138–140°C; **2**, 127–131°C; **3**, 195–197°C.

X-ray Crystallography

Dark red crystals of **1**, **2**, and **3** suitable for x-ray diffraction studies were obtained by slow evaporation of saturated solutions of the compounds in acetone/ethanol mixtures at ambient temperature. Unit cell parameters were determined from 20–25 well-centered, intense reflections in the range $15° \leq 2\theta \leq 30°$. A Siemens (Bruker) R3m diffractometer in the $\omega/2\theta$ mode (for **1** and **2**) or $\theta/2\theta$ mode (for **3**) with variable scan speed (3–20 deg min^{-1} for **1** and **3**; 2–20 deg min^{-1} for **2**) and graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å) was used to collect the intensity data at ambient temperature. No decay was observed over the course of the data collections. For each crystal, data were corrected for background, attenuators, Lorentz and polarization effects in the usual fashion, but not for absorption [19].

Structure solutions and full-matrix least-squares refinements were accomplished with the SHELXTL Plus package of programs. Heavy atoms were located *via* direct methods for **1** and **3** and Patterson methods for **2**. Atomic scattering factors were from the literature [20] and anomalous dispersion was applied to all non-hydrogen atoms. For **1**, only Ce and O atoms were refined anisotropically, while for **2** and **3**, Ce, O, and C atoms of methyl groups were refined anisotropically. Rotational disorder in peripheral hydrocarbyl substituents was not modelled. Hydrogen atom positions were calculated geometrically, fixed at a C–H distance of 0.96 Å, and not refined. Crystal data and further data collection parameters for **1**, **2**, and **3** are summarized in Table I.

TABLE I Crystallographic data and parameters for **1**, **2**, and **3**

Compound	**1**	**2**	**3**
Formula	$C_{40}H_{68}CeO_8$	$C_{44}H_{76}CeO_8$	$C_{44}H_{76}CeO_8$
MW	817.1	873.2	873.2
Cryst. syst.	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2/c$	$P\bar{1}$
a(Å)	13.003 (4)	22.790 (10)	12.398 (3)
b(Å)	35.136 (14)	11.900 (4)	19.838 (4)
c(Å)	30.231 (11)	19.499 (7)	21.321 (4)
α(°)	90	90	97.40 (2)
β(°)	90.98 (3)	105.48 (3)	89.91 (2)
γ(°)	90	90	106.45 (2)
V(Å^3)	13810 (9)	5096 (4)	4984 (2)
Z	12	4	4
D_C(g cm^{-3})	1.179	1.138	1.164
F(000)	5160	1848	1848
2θ($_{max}$°)	40	40	45
Tot. reflns	13136	4928	13349
Unique reflns	12819	4716	12945
Obsd reflns	5840[a]	2019[a]	10780[a]
μ(cm^{-1})	10.31	9.35	9.56
N_V	724	359	755
R[b]	0.0695	0.0980	0.0536
R_w[b]	0.0679	0.0965	0.0618
GOF[C]	1.92	4.21	2.79

[a] $F > 6.0\sigma(F)$

[b] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o) + g \times (F_o)^2$; $g = 0.0005$, 0.0002, and 0.0005 for **1**, **2**, and **3**, respectively.

[c] $GOF = [\sum w(|F_o| - F_c|^2/(NO - NV)]^{1/2}$, where NO is the number of observations and NV is the number of variables.

RESULTS AND DISCUSSION

Preparation

The complexes, Ce(txhd)$_4$ (**1**), Ce(tmod)$_4$ (**2**), and Ce(tmhd)$_4$ (**3**), were easily prepared by the interaction of the sodium salt of the β-diketonate with $Ce(NO_3)_3 \cdot 6H_2O$ in aqueous ethanol using a modification of literature procedures [21–25]. Homoleptic Ce(IV) β-diketonate complexes have also been synthesized from ceric ammonium nitrate [14] and $CeCl_3 \cdot 7H_2O$ [13] starting materials. In the present case, purification of complexes **1** and **3** was effected by sublimation.

Thermal Studies

The thermal behavior of the cerium complexes was investigated using TGA. The onset of sublimation for **1** occurred at ~ 117°C, with the rate of maximum weight loss at ~ 199°C. The corresponding thermal parameters for **3** were ~ 114°C and 233°C, respectively. A residue of ~ 8–10% remained after the sublimation of **1**, as compared to < 1% residue for **3**.

Sublimation of **2** could not be accomplished without apparent decomposition. Upon heating in an evacuated sublimation apparatus, **2** melted and bubbled to form a viscous liquid, which darkened upon solidification at room temperature. This residue was not soluble in the usual solvents and was not studied further. TGA for **2** showed a maximum rate of weight loss at 180°C, followed by slower, very gradual weight loss at higher temperatures. Approximately 25–30% of the mass remained, even at very high temperatures. We also note that dark-red crystals of **2** were observed to decompose to a pale yellow material over several months when stored under air in a sealed vial at ambient temperature; crystals of **1** and **3** remained unchanged over the same time period under the same conditions.

DSC studies of **1** and **3** showed the expected endotherm for melting and exotherm for decomposition. The onset temperature for decomposition of **1** was ~307°C, while that for **3** was ~ 278°C. Although the DSC trace for **2** displayed a melting point, there was little evidence for an exotherm at lower temperatures where the compound decomposed under bulk sublimation conditions and where weight loss occurred in the TGA experiment; a large exotherm, presumably associated with decomposition, was initiated at 380°C.

X-ray Diffraction Studies

The asymmetric unit of the unit cell for **1** contains three crystallographically independent molecules of Ce(txhd)$_4$, hereafter designated **1a–c** (Fig. 1 depicts the structure of **1b**). The assignment of the coordination polyhedra about the Ce atoms is facilitated by calculation of the δ angles [26–28]. The values of these angles for the D_{2d} dodecahedron are $\delta_1=\delta_2=\delta_3=\delta_4=29.5°$ while for the C_{2v} bicapped trigonal prism the values are $\delta_1=0.0°$, $\delta_2=21.8°$, $\delta_3=\delta_4=48.2°$ and for the D_{4d} square antiprism

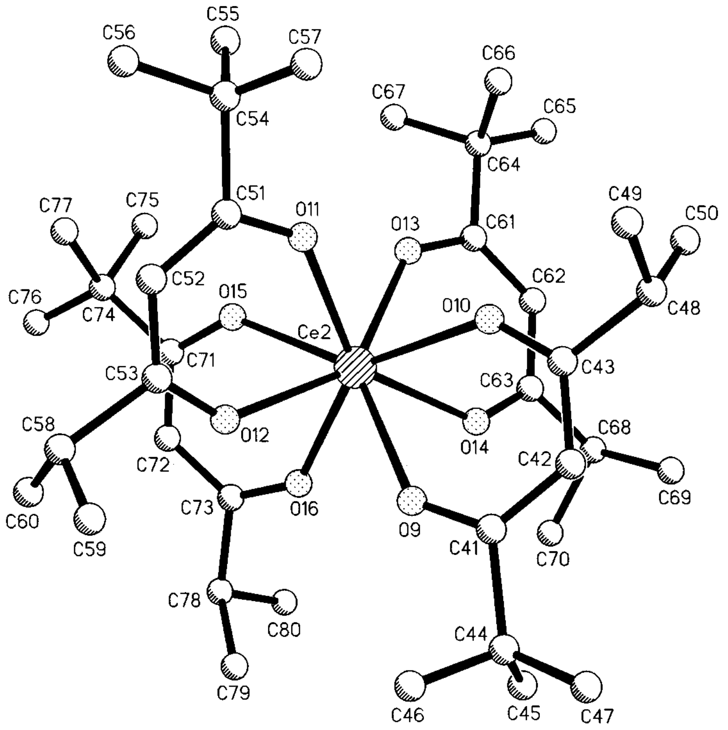

FIGURE 1 Molecular structure and atom numbering scheme for **1b**. Hydrogen atoms and thermal ellipsoids are not illustrated for clarity.

$\delta_1 = \delta_2 = 0.0°$, $\delta_3 = \delta_4 = 52.4°$. Applying the literature method for the calculation of the δ angles in the case of **1a–c**, we find values of 0.7, 0.7, 51.9, and 50.6° for **1a** (using atoms O(2), O(4), O(6), and O(8) to describe the shape), 2.8, 3.2, 51.0, and 50.3° for **1b** (using atoms O(11), O(12), O(14), and O(15)), and 0.2, 0.0, 51.8, and 48.6° for **1c** (using atoms O(18), O(20), O(21), and O(24)). Thus, the general shape or coordination polyhedron around each Ce atom in **1a–c** is probably best described as an "intermediate stereochemistry" based on a square antiprism of the D_2 type [29].

This sort of structure, in which opposite sides of the square faces of the antiprism are spanned by the terminal donor atoms for two of the chelating ligands, has been designated D_2(*ssss*) [26,30]. Since the chelate ligand in **1** is unsymmetrical, the possibility of geometrical isomers must be considered. Troyanov has discussed the situation for the D_2(*ssss*) qeometry [30]. He labeled the isomers as *trans-trans*, *cis-cis*, and *cis-trans*; the *trans* and *cis* labels refer to the stereochemical disposition of the two chelate rings in each of the square faces of the D_2 square antiprism. Two other geometrical isomers, not enumerated previously, are possible [30], which we designate as *cis-cis 2* and *cis-trans 2* (Fig. 2). For **1**, the stereochemistry for **1a** of the asymmetric unit corresponds to the *trans-trans* geometry (Fig. 2), while independent molecules **1b** and **1c** can be considered to adopt the *cis-trans* geometry. The *trans-trans* and *cis-trans* geometrical isomers also cocrystallized in the case of CeL_4 (L = 2,6,6-trimethyl-2-methoxy-3,5-heptanedionate) [30].

Bond lengths and angles within the coordination spheres of **1a–c** are collected in Table II. The Ce–O bond distances range from 2.27(1)–2.37(1) Å in **1a**, 2.30(1)–2.33(1) Å in **1b**, 2.29(1)–2.36(1) Å in **1c**; the average Ce–O bond length is

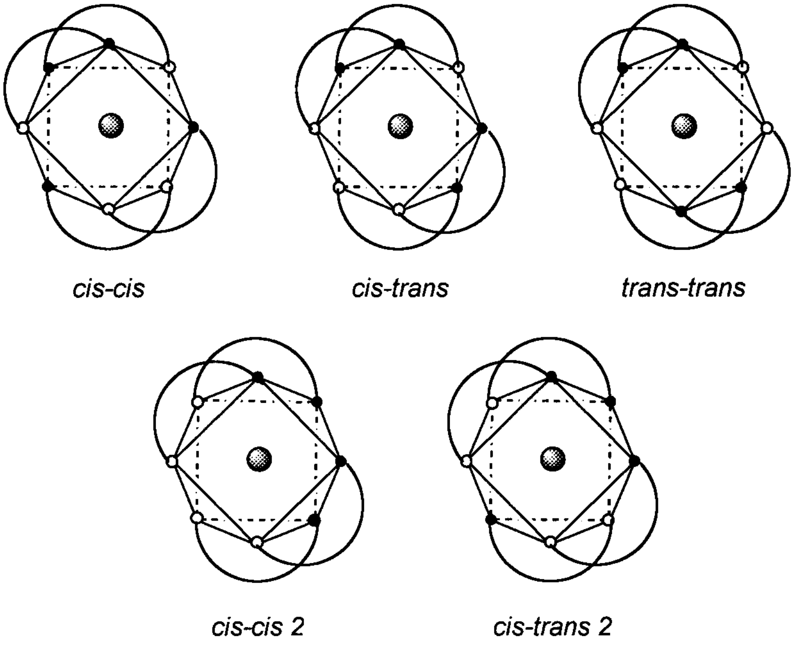

FIGURE 2 Schematic representations of possible geometrical isomers for the D_2(*ssss*) square antiprism having four unsymmetrical chelate ligands of the same composition. The large circle in the center represents the cerium atom, while the inequivalent oxygen atoms are represented by the small open and darkened circles.

TABLE II Selected bond lengths(Å) and angles(°) for **1a–c**

Molecule **1a**			
Ce(1)–O(1)	2.31(2)	Ce(1)–O(2)	2.32(1)
Ce(1)–O(3)	2.30(1)	Ce(1)–O(4)	2.29(2)
Ce(1)–O(5)	2.27(1)	Ce(1)–O(6)	2.33(2)
Ce(1)–O(7)	2.28(2)	Ce(1)–O(8)	2.37(1)
O(1)–Ce(1)–O(2)	72.6(6)	O(1)–Ce(1)–O(3)	113.4(5)
O(2)–Ce(1)–O(3)	73.2(5)	O(1)–Ce(1)–O(4)	72.5(6)
O(2)–Ce(1)–O(4)	114.2(6)	O(3)–Ce(1)–O(4)	72.3(6)
O(1)–Ce(1)–O(5)	80.6(6)	O(2)–Ce(1)–O(5)	144.4(5)
O(3)–Ce(1)–O(5)	140.5(5)	O(4)–Ce(1)–O(5)	78.0(6)
O(1)–Ce(1)–O(6)	143.6(5)	O(2)–Ce(1)–O(6)	141.7(5)
O(3)–Ce(1)–O(6)	77.8(5)	O(4)–Ce(1)–O(6)	79.1(6)
O(5)–Ce(1)–O(6)	71.5(5)	O(1)–Ce(1)–O(7)	140.2(6)
O(2)–Ce(1)–O(7)	76.8(6)	O(3)–Ce(1)–O(7)	80.3(5)
O(4)–Ce(1)–O(7)	145.0(5)	O(5)–Ce(1)–O(7)	113.2(5)
O(6)–Ce(1)–O(7)	74.1(5)	O(1)–Ce(1)–O(8)	77.8(5)
O(2)–Ce(1)–O(8)	77.6(5)	O(3)–Ce(1)–O(8)	143.1(5)
O(4)–Ce(1)–O(8)	142.0(5)	O(5)–Ce(1)–O(8)	74.2(5)
O(6)–Ce(1)–O(8)	114.9(5)	O(7)–Ce(1)–O(8)	71.2(5)
Molecule **1b**			
Ce(2)–O(9)	2.33(1)	Ce(2)–O(10)	2.33(2)
Ce(2)–O(11)	2.31(1)	Ce(2)–O(12)	2.31(1)
Ce(2)–O(13)	2.30(1)	Ce(2)–O(14)	2.33(1)
Ce(2)–O(15)	2.31(1)	Ce(2)–O(16)	2.32(1)
O(9)–Ce(2)–O(10)	71.1(5)	O(9)–Ce(2)–O(11)	115.1(5)
O(10)–Ce(2)–O(11)	73.7(5)	O(9)–Ce(2)–O(12)	73.8(5)
O(10)–Ce(2)–O(12)	112.4(6)	O(11)–Ce(2)–O(12)	72.0(5)
O(9)–Ce(2)–O(13)	140.6(5)	O(10)–Ce(2)–O(13)	80.0(5)
O(11)–Ce(2)–O(13)	80.1(5)	O(12)–Ce(2)–O(13)	143.9(5)
O(9)–Ce(2)–O(14)	75.8(5)	O(10)–Ce(2)–O(13)	78.1(5)
O(11)–Ce(2)–O(14)	143.5(5)	O(12)–Ce(2)–O(14)	141.8(5)
O(13)–Ce(2)–O(14)	72.5(5)	O(9)–Ce(2)–O(15)	142.2(5)
O(10)–Ce(2)–O(15)	144.5(6)	O(11)–Ce(2)–O(15)	78.1(5)
O(12)–Ce(2)–O(15)	77.8(5)	O(13)–Ce(2)–O(15)	74.3(5)
O(14)–Ce(2)–O(15)	115.6(5)	O(9)–Ce(2)–O(16)	80.0(5)
O(10)–Ce(2)–O(16)	143.6(5)	O(11)–Ce(2)–O(16)	140.5(5)
O(12)–Ce(2)–O(16)	78.7(6)	O(13)–Ce(2)–O(16)	112.0(5)
O(14)–Ce(2)–O(16)	73.7(5)	O(15)–Ce(2)–O(16)	70.2(5)
Molecule **1c**			
Ce(3)–O(17)	2.29(1)	Ce(3)–O(18)	2.36(2)
Ce(3)–O(19)	2.32(1)	Ce(3)–O(20)	2.33(2)
Ce(3)–O(21)	2.29(2)	Ce(3)–O(22)	2.31(2)
Ce(3)–O(23)	2.31(1)	Ce(3)–O(24)	2.34(1)
O(17)–Ce(3)–O(18)	71.1(5)	O(17)–Ce(3)–O(19)	139.7(6)
O(18)–Ce(3)–O(19)	77.5(5)	O(17)–Ce(3)–O(20)	77.1(5)
O(18)–Ce(3)–O(20)	78.1(5)	O(19)–Ce(3)–O(20)	72.0(5)
O(17)–Ce(3)–O(21)	145.2(6)	O(18)–Ce(3)–O(21)	142.2(6)
O(19)–Ce(3)–O(21)	72.6(6)	O(20)–Ce(3)–O(21)	113.0(6)
O(17)–Ce(3)–O(22)	80.6(5)	O(18)–Ce(3)–O(22)	143.1(6)
O(19)–Ce(3)–O(22)	113.2(6)	O(20)–Ce(3)–O(22)	72.7(5)
O(21)–Ce(3)–O(22)	71.9(6)	O(17)–Ce(3)–O(23)	112.9(5)
O(18)–Ce(3)–O(23)	74.9(6)	O(19)–Ce(3)–O(23)	81.6(5)
O(20)–Ce(3)–O(23)	145.6(5)	O(21)–Ce(3)–O(23)	78.2(6)
O(22)–Ce(3)–O(23)	139.8(6)	O(17)–Ce(3)–O(24)	73.3(6)
O(18)–Ce(3)–O(24)	114.4(5)	O(19)–Ce(3)–O(24)	144.8(6)
O(20)–Ce(3)–O(24)	141.1(5)	O(21)–Ce(3)–O(24)	80.4(6)
O(22)–Ce(3)–O(24)	77.9(5)	O(23)–Ce(3)–O(24)	71.0(5)

2.31 Å. These values are comparable to those found for other homoleptic Ce(IV) β-diketonate complexes [12,14,30–38] and are considerably shorter than those for neutral and anionic Ce(III) β-diketonate complexes [11,12,15,39]. There are no discernible differences in bonding parameters among the different independent molecules of the asymmetric unit of **1**.

The asymmetric unit for **2** contains two crystallographically independent halves of molecules of Ce(tmod)$_4$, hereafter designated **2a** and **2b** (Fig. 3 depicts the structure of **2b**); each Ce atom of the asymmetric unit is situated on a two-fold axis [40]. The δ angles for **2a** and **2b** are 4.8, 4.8, 51.8, 54.1° (using atoms O(1), O(3), O(2a), and O(4a) to describe the shape) and 1.9, 1.9, 50.6, and 51.3° (using atoms O(5), O(7), O(6a), an O(8a)), respectively. Again, the shapes of the molecules are best described as D_2(*ssss*) square antiprismatic. Both independent molecules of Cu(tmod)$_2$ have the *trans-trans* geometry. Bond lengths and angles within the coordination spheres of **2a** and **2b** are collected in Table III. The Ce–O bond distances range from 2.24(2)–2.37(2) Å in **2a** and 2.22(2)–2.38(2) Å in **2b**; the average Ce–O bond length is 2.26 Å. The rather poor quality of the crystal and high thermal motion resulted in the inability to model rotational disorder in the side chains; these problems are reflected in the larger standard deviations in structural parameters for **2a** and **2b**.

The asymmetric unit for **3** contains two crystallographically independent molecules of Ce(tmhd)$_4$, hereafter designated **3a** and **3b** (Fig. 4 depicts the structure of **3b**). The δ angles for **3a** and **3b** are 5.4, 10.1, 53.3, and 54.1° (using atoms O(1), O(4), O(6),

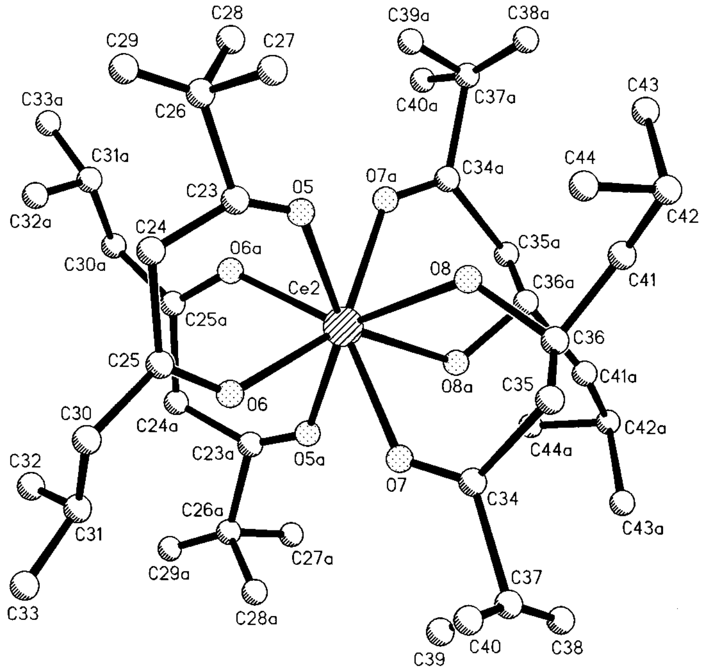

FIGURE 3 Molecular structure and atom numbering scheme for **2b**. Hydrogen atoms and thermal ellipsoids are not illustrated for clarity.

TABLE III Selected bond lengths(Å) and angles(°) for **2**

Molecule **2a**			
Ce(1)–O(1)	2.24(2)	Ce(1)–O(2)	2.37(2)
Ce(1)–O(3)	2.30(2)	Ce(1)–O(4)	2.24(2)
O(1)–Ce(1)–O(2)	73.8(8)	O(1)–Ce(1)–O(3)	114.0(7)
O(2)–Ce(1)–O(3)	71.7(8)	O(1)–Ce(1)–O(4)	69.0(7)
O(2)–Ce(1)–O(4)	110.3(8)	O(3)–Ce(1)–O(4)	73.0(8)
O(1)–Ce(1)–O(1a)	142.3(9)	O(2)–Ce(1)–O(1a)	77.5(7)
O(3)–Ce(1)–O(1a)	78.6(7)	O(4)–Ce(1)–O(1a)	145.7(7)
O(2)–Ce(1)–O(2a)	79.8(12)	O(3)–Ce(1)–O(2a)	143.8(8)
O(4)–Ce(1)–O(2a)	139.7(8)	O(3)–Ce(1)–O(3a)	142.5(10)
O(4)–Ce(1)–O(3a)	80.1(8)	O(4)–Ce(1)–O(4a)	87.4(10)
Molecule **2b**			
Ce(2)–O(5)	2.29(3)	Ce(2)–O(6)	2.22(2)
Ce(2)–O(7)	2.32(2)	Ce(2)–O(8)	2.38(2)
O(5)–Ce(2)–O(6)	78.7(8)	O(5)–Ce(2)–O(7)	115.5(9)
O(6)–Ce(2)–O(7)	71.6(8)	O(5)–Ce(2)–O(8)	67.6(8)
O(6)–Ce(2)–O(8)	113.5(7)	O(7)–Ce(2)–O(8)	74.1(8)
O(5)–Ce(2)–O(5a)	150.4(11)	O(6)–Ce(2)–O(5a)	78.7(8)
O(7)–Ce(2)–O(5a)	74.6(9)	O(8)–Ce(2)–O(5a)	140.1(8)
O(6)–Ce(2)–O(6a)	79.8(12)	O(7)–Ce(2)–O(6a)	143.9(8)
O(8)–Ce(2)–O(6a)	139.3(8)	O(7)–Ce(2)–O(7a)	142.6(10)
O(8)–Ce(2)–O(7a)	77.8(8)	O(8)–Ce(2)–O(8a)	82.0(9)

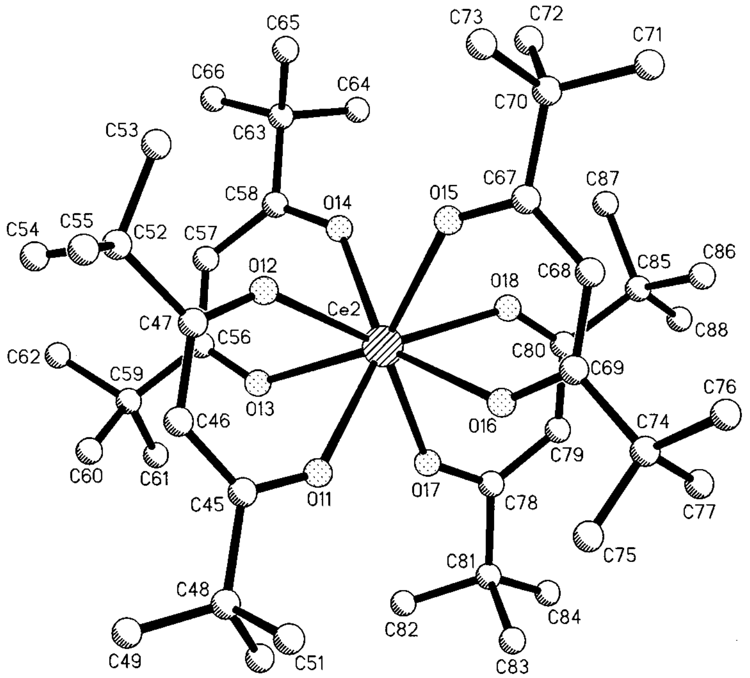

FIGURE 4 Molecular structure and atom numbering scheme for **3b**. Hydrogen atoms and thermal ellipsoids are not illustrated for clarity.

and O(7) to describe the shape) and 4.2, 10.7, 53.2, and 53.3° (using atoms O(11), O(14), O(15), and O(17)), respectively. The coordination polyhedra are somewhat more irregular here, but are probably still best considered as $D_2(ssss)$ square antiprismatic. There is, however, some distortion along the reaction path toward bicapped trigonal prismatic geometry.

We note that the triclinic form of **3**, β-[Ce(tmhd)$_4$], has previously been studied at low temperature (150 K), where the shapes of the two independent molecules were described as "distorted dodecahederal" [14]. In both the present and previous report [14], the positions of the Ce(1) and Ce(2) atoms correspond identically, which facilitates the discussion. We calculate the δ angles for the two independent molecules of **3** at low temperature, based on the published coordinates [14], to be 5.7, 9.3, 45.7, and 46.5° (**3a** at low temperature using atoms O(2), O(3), O(5), and O(8) to describe the shape) and 4.2, 10.7, 53.2, and 53.3° (**3b** at low temperature, using atoms O(10), O(11), O(14), and O(15)). At low temperature, the δ angles for **3a** are clearly different than those calculated for the room temperature structure (*vide supra*), even given the somewhat larger standard deviations for structural parameters involved in the higher temperature structure determination. These data suggest an assignment of distorted bicapped trigonal prismatic geometry at 150 K, with O(4) and O(6) as the capping atoms, rather than a dodecahedral or square antiprismatic geometry. On the other hand, **3b** has essentially the same distorted $D_2(ssss)$ square antiprismatic shape at the two temperatures. Subtle changes in the unit cell parameters as a function of temperature, including the shrinking of all unit cell lengths and small changes in some of the unit cell angles, are likely the result of the change in conformation of **3a**. We emphasize that there are only small energy differences between the different polyhedral geometries for eight-coordinate complexes and that the definitive assignment of a particular geometry, especially in distorted cases, is problematic [26–29,41,42]. Apparently, the temperature difference in the two structural determinations was enough to cause the conformational change observed in complex **3a**.

Bond lengths and angles within the coordination spheres of **3a** and **3b** are collected in Table IV. The Ce–O bond distances range from 2.289(5)–2.345(4) Å in **3a** and 2.292(4)–2.340(4) Å in **3b**; the average Ce–O bond length is 2.319 Å. These values are comparable to those found for monoclinic α-[Ce(tmhd)$_4$ (Ce–O range 2.29(1)–2.37(1) Å; average 2.32 Å) [38] and triclinic β-[Ce(tmhd)$_4$] at low temperature (Ce–O range 2.300(5)–2.367(5) Å; average 2.334 Å) [14].

Examination of the crystal packing suggests one possible explanation for why **1** and **3** sublime readily, while **2** does not. Despite a slightly lower density, there are several intermolecular contacts in the range 3.23–3.74 Å for **2**, while in **1** and **3**, there are no significant intermolecular contacts at < 3.80 Å. Interestingly, CeL_4 (L = 1-phenyl-5-methyl-1,3-hexanedionato), which has intermolecular contacts as small as 3.36 Å, also does not sublime [14]. Like **2**, this compound was observed to decompose to a black residue upon attempted sublimation [14]. The closer intermolecular contacts in the solid state for these latter two compounds, though weak, may reduce the volatility sufficiently so that either melting and/or decomposition occurs instead. Alternatively, it is possible that the presence of an *iso*-butyl group generally confers deleterious properties to potential Ce(IV) CVD precursors. For example, the *iso*-butyl substituent may be readily oxidized in the melt by the Ce(IV) centers, leading to irreversible decomposition.

TABLE IV Selected bond lengths(Å) and angles(°) for **3**

Molecule **3a**			
Ce(1)–O(1)	2.300(4)	Ce(1)–O(2)	2.332(4)
Ce(1)–O(3)	2.344(5)	Ce(1)–O(4)	2.289(5)
Ce(1)–O(5)	2.345(4)	Ce(1)–O(6)	2.320(5)
Ce(1)–O(7)	2.318(4)	Ce(1)–O(8)	2.310(4)
O(1)–Ce(1)–O(2)	70.2(1)	O(1)–Ce(1)–O(3)	80.4(2)
O(2)–Ce(1)–O(3)	77.0(2)	O(1)–Ce(1)–O(4)	79.6(2)
O(2)–Ce(1)–O(4)	138.2(2)	O(3)–Ce(1)–O(4)	69.8(2)
O(1)–Ce(1)–O(5)	74.3(2)	O(2)–Ce(1)–O(5)	118.5(1)
O(3)–Ce(1)–O(5)	142.1(2)	O(4)–Ce(1)–O(5)	78.0(2)
O(1)–Ce(1)–O(6)	107.9(2)	O(2)–Ce(1)–O(6)	75.5(2)
O(3)–Ce(1)–O(6)	146.2(2)	O(4)–Ce(1)–O(6)	143.1(2)
O(5)–Ce(1)–O(6)	70.0(2)	O(1)–Ce(1)–O(7)	143.4(1)
O(2)–Ce(1)–O(7)	77.6(1)	O(3)–Ce(1)–O(7)	75.7(2)
O(4)–Ce(1)–O(7)	116.4(2)	O(5)–Ce(1)–O(7)	138.8(2)
O(6)–Ce(1)–O(7)	79.5(2)	O(1)–Ce(1)–O(8)	145.6(2)
O(2)–Ce(1)–O(8)	142.6(2)	O(3)–Ce(1)–O(8)	111.8(2)
O(4)–Ce(1)–O(8)	75.4(2)	O(5)–Ce(1)–O(8)	77.7(1)
O(6)–Ce(1)–O(8)	80.2(2)	O(7)–Ce(1)–O(8)	70.2(1)
Molecule **3b**			
Ce(2)–O(11)	2.336(4)	Ce(2)–O(12)	2.297(6)
Ce(2)–O(13)	2.331(5)	Ce(2)–O(14)	2.315(4)
Ce(2)–O(15)	2.336(5)	Ce(2)–O(16)	2.292(4)
Ce(2)–O(17)	2.306(6)	Ce(2)–O(18)	2.340(5)
O(11)–Ce(2)–O(12)	70.6(2)	O(11)–Ce(2)–O(13)	76.7(2)
O(12)–Ce(2)–O(13)	79.1(2)	O(11)–Ce(2)–O(14)	140.3(2)
O(12)–Ce(2)–O(14)	82.4(2)	O(13)–Ce(2)–O(14)	69.9(2)
O(11)–Ce(2)–O(15)	118.2(2)	O(12)–Ce(2)–O(15)	73.7(2)
O(13)–Ce(2)–O(15)	141.0(2)	O(14)–Ce(2)–O(15)	79.1(1)
O(11)–Ce(2)–O(16)	73.5(2)	O(12)–Ce(2)–O(16)	106.5(2)
O(13)–Ce(2)–O(16)	145.4(2)	O(14)–Ce(2)–O(16)	144.0(2)
O(15)–Ce(2)–O(16)	70.7(2)	O(11)–Ce(2)–O(17)	79.7(2)
O(12)–Ce(2)–O(17)	144.7(2)	O(13)–Ce(2)–O(17)	75.8(2)
O(14)–Ce(2)–O(17)	111.1(2)	O(15)–Ce(2)–O(17)	139.4(2)
O(16)–Ce(2)–O(17)	81.9(2)	O(11)–Ce(2)–O(18)	141.3(2)
O(12)–Ce(2)–O(18)	145.0(2)	O(13)–Ce(2)–O(18)	116.2(2)
O(14)–Ce(2)–O(18)	75.0(2)	O(15)–Ce(2)–O(18)	76.0(2)
O(16)–Ce(2)–O(18)	79.1(2)	O(17)–Ce(2)–O(18)	69.7(2)

CONCLUSIONS

We have demonstrated that unsymmetrical, nonfluorinated β-diketonates (L) as ancillary ligands for Ce(IV) is a viable approach for increasing the volatility of the homoleptic complexes, CeL_4, as well as for attenuating their decomposition temperatures. Ce(txhd)$_4$ sublimes over 30°C lower than Ce(tmhd)$_4$, but decomposes at a somewhat higher temperature than the latter complex. The ability to vary these operational temperatures is desirable for flexibility in MOCVD processing.

The solid-state structures of complexes **1**, **2**, and **3** at room temperature all have significant thermal motion in the side chains, consistent with inefficient packing of the molecules. However, it appears that Ce(IV) complexes having ligands that contain an *iso*-butyl peripheral substituent, such as **2**, do not have sufficient stability or volatility to have utility for CVD applications.

The solid-state coordination polyhedral shape for all three complexes is best described as based on the $D_2(ssss)$ square antiprism. Complexes **1** and **2** have unsymmetrical chelate ligands; as such, five geometrical isomers are possible for the $D_2(ssss)$ shape. The asymmetric unit of **1** contains three independent molecules, of which two of the five possible geometrical isomers are found, namely the *trans*-*trans* and one of the two *cis*-*trans* isomers. The two independent molecules for **2** both adopt the *trans*-*trans* configuration. Complex **3** crystallized in the triclinic (β) form, which had previously been studied at low temperature [14]. Our room temperature determination shows that one of the two crystallographically independent molecules undergoes a significant change in geometry as a function of temperature from $D_2(ssss)$ square antiprismatic at room temperature to what is probably best described as bicapped trigonal prismatic at 150 K. This result illustrates the small energy differences that exist between the different eight-coordinate geometries.

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Supplementary Material

Full lists of crystallographic data for **1** (CCDC 148160), **2** (CCDC 148161), and **3** (CCDC 148162), including atomic coordinates, bond lengths and angles, and anisotropic thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. Tables of observed and calculated structure factors are available from the authors upon request.

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