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Synthesis and X-ray Structure of the First Divalent Lanthanide Acetylacetonate Complex, Bis(2,2,6,6-tetramethylheptane-3,5-dionato)bis(dimethoxyethane)europium(II)

William J. Evans,* Julie L. Shreeve, and Joseph W. Ziller

Department of Chemistry, University of California,
Irvine, California 92717

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Introduction

β-Diketonates have been studied extensively as ligands in lanthanide chemistry, and their trivalent lanthanide complexes have been utilized in applications ranging from polymerization catalysis[1,2] to chemical vapor deposition (CVD)[3,4] to use as NMR shift reagents.[5] Despite the broad development of lanthanide β-diketonate chemistry, no structurally characterized examples of β-diketonate complexes have been reported with the divalent lanthanides. Given the variety of substituted β-diketonates available, this ligand system can provide many opportunities for adjusting the coordination environment of the divalent metals. Since divalent lanthanides can display unusual chemical reactivity[6] and since divalent lanthanide β-diketonates could have charge to radius ratios unattainable in trivalent β-diketonate complexes, exploration of this area seemed warranted. We report here the synthesis of the first structurally characterized divalent lanthanide β-diketonate complex, $(THD)_2Eu(DME)_2$, **1**, (THD = 2,2,6,6-tetramethylheptane-3,5-dionate; DME = dimethoxyethane). The formation of the Sm(II) analog, $(THD)_2Sm(DME)_2$, **2**, and its decomposition product, $(THD)_3Sm(DME)$, **3**, are also described.

Experimental Section

All compounds described below were handled under nitrogen with rigorous exclusion of air and water using standard Schlenk, vacuum line, and glovebox techniques. Solvents and dimethoxyethane were freshly dried and distilled from sodium benzophenone as previously described.[7] Lanthanide trichlorides were dried as previously described.[8] K(THD) was prepared from the reaction of KH and 2,2,6,6-tetramethylheptane-3,5-dione (Aldrich) in THF. $EuI_2(THF)_2$[9] and $SmI_2(THF)_2$[10] were prepared from the reaction of Eu or Sm metal (Rhône Poulenc) and diiodoethane (Aldrich) in THF. NMR spectra were recorded on a General Electric QE300 instrument. Infrared spectra were recorded on a Perkin Elmer 1600 series FT-IR. Elemental analysis was performed by Analytische Laboratorien GmbH, D-51647 Gummersbach, Germany. Complexometric metal analysis was done as previously described.[7]

$Eu(THD)_2(DME)_2$, 1. In a glovebox, K(THD) (606 mg, 2.72 mmol) was added to a slurry of $EuI_2(THF)_2$ (750 mg, 1.36 mmol) in 15 mL of THF. The reaction mixture turned orange. The reaction mixture was stirred 18 h and centrifuged to yield a red-orange solution and a white solid (462 mg). The supernatant was dried by rotary evaporation, extracted with toluene and dried to give an oily red material. Dissolution of this red material in DME (*ca.* 3 mL) and subsequent drying by rotary evaporation yielded **1** as a orange-red solid. (939 mg, 1.34 mmol, 98%) IR (neat): 2956 s br, 2936 s, 2868 s, 1573 s br, 1537 s, 1503 s, 1451 s, 1402 s br, 1358 s, 1281 w, 1244 m, 1225 m, 1182 m, 1137 m 1072 w, 1047 w, 1026 w, 954 w, 931 w, 889 w, 868 s, 820 w, 792 m, 758 m, 734 m, 599 w cm^{-1}. Anal. Calcd for $EuC_{30}H_{58}O_8$: Eu, 21.75; C, 51.56; H, 8.37. Found: Eu, 21.40; C, 51.32; H, 8.21.

$Sm(THD)_2(DME)_2$, 2. In a glovebox, a 200 mg samarium metal piece was added to $SmI_2(THF)_2$ (500 mg, 0.912 mmol) dissolved in 15 mL of THF. K(THD) (406 mg, 1.82 mmol) was added and the reaction mixture was stirred for 18 h. The reaction was centrifuged to yield a dark purple-brown solution and a white solid (299 mg). The supernatant was dried by rotary evaporation, extracted with toluene, and dried to give a dark sticky material. Dissolution of this material in DME (*ca.* 4 mL) and subsequent drying by rotary evaporation yielded **2** as a dark purple-brown solid (617 mg, 0.885 mmol, 97%). Solutions of **2** are best stored in the presence of a small piece of samarium metal to minimize formation of **3**.[10] ^1H NMR(C_6D_6): δ 6.84 (2H, CH), 2.83 (8H, OCH_2), 1.90 (12H, OCH_3), 1.23 (36H, Me). IR (neat): 2986 s br, 2932 s, 2860 s, 1576 s br, 1537 s, 1502 s, 1455 s, 1406 s br, 1352 s, 1280 w, 1238 m, 1220 m, 1178 m, 1136 m, 1070 w, 1035 w, 957 w, 926 w, 915 w, 861 s, 819 w, 795 m, 759 m, 735 m, 687 w, 597 w cm^{-1}. Anal. Calcd for $SmC_{30}H_{58}O_8$: Sm, 21.57. Found: Sm, 21.4.

$Sm(THD)_3(DME)$, 3. Colorless crystals of **3** formed from a concentrated THF/DME/toluene solution of **2** at −34 °C after approximately 2 weeks. ^1H NMR(C_6D_6): δ 6.86 (3H, CH), 2.82 (4H, OCH_2), 2.27 (6H, OCH_3), 1.25 (54H, Me). IR (neat): 2956 s br, 2901 s, 2864 s, 1589 s, 1570 s br, 1552 s, 1538 s, 1502 s, 1452 s, 1407 s br, 1383 s, 1356 s, 1284 w, 1242 m, 1220 m, 1179 m, 1138 m, 1074 w, 1037 w, 959 w, 936 w, 910 w, 864 s, 819 w, 791 m, 759 m, 737 m, 598 w cm^{-1}.

General Aspects of X-ray Data Collection, Structure Determination, and Refinement for 1 and 3. In each case a crystal was immersed in Paratone-D oil[11] under nitrogen and then manipulated in air onto a glass fiber and transferred to the nitrogen stream of a Syntex $P2_1$ diffractometer equipped with a modified LT-1 low-temperature system or a Siemens P3 diffractometer (Siemens R3m/V System) equipped with a modified LT-2 low-temperature system. The determination of Laue symmetry, crystal class, unit cell parameters and the crystal's orientation matrix were carried out using standard techniques similar to those of Churchill.[12] All data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. Any reflection with $I(\text{net}) < 0$ was assigned the value $|F_o| = 0$. All crystallographic calculations were carried out using either our locally modified version of the UCLA Crystallographic Computing Package[13] or the SHELXTL PLUS program set.[14] The analytical scattering factors for neutral atoms were used throughout the analysis,[15] both the real ($\Delta f'$) and imaginary ($i\delta f''$) components of anomalous dispersion were included. The quantity

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Table 1. Experimental Data for the X-ray Diffraction Studies of $(THD)_2Eu(DME)_2$, **1**, and $(THD)_3Sm(DME)$, **3**[a]

	1	**3**
formula	$EuC_{30}H_{58}O_8$	$SmC_{37}H_{67}O_8$
fw	698.7	790.3
temp (K)	158	158
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	10.4491(11)	10.693(2)
b (Å)	23.096(3)	13.459(3)
c (Å)	14.499(2)	16.004(3)
α (deg)		71.332(14)
β (deg)	95.188(9)	75.691(14)
γ (deg)		77.211(15)
V (Å^3)	3484.8(7)	2088.8(7)
Z	4	2
D_{calcd} (Mg/m^3)	1.332	1.256
diffractometer	Siemens P3	Siemens P3
data collcd	$+h,+k,\pm l$	$+h,\pm k,\pm l$
scan type	$\theta-2\theta$	$\theta-2\theta$
scan range (deg)	1.20 plus Kα separation	1.20 plus Kα separation
scan speed (deg min^{-1} (in ω))	constant, 3.00	constant, 3.00
2θ range (deg)	4.0 to 45.0	4.0 to 45.0
μ(MoKα) (mm^{-1})	1.841	1.448
abs cor	semiempirical (φ-scan method)	semiempirical (φ-scan method)
no. of reflns collcd	5022	5864
X; no. of reflcns with ($\lvert F_o\rvert > X\sigma(\lvert F_o\rvert)$)	X = 3.0; 3953	X = 4.0; 5249
no. of variables	352	416
R_F	3.7%	3.3%
R_{wF}	4.3%	5.0%
goodness of fit	1.91	1.99

[a] Radiation: Mo Kα ($\bar{\lambda}$ = 0.710 730 Å). Monochromator: highly oriented graphite.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $(THD)_2Eu(DME)_2$, **1**

Eu(1)−O(1)	2.448(4)	Eu(1)−O(5B)	2.706(25)
Eu(1)−O(2)	2.500(4)	Eu(1)−O(6)	2.711(4)
Eu(1)−O(3)	2.496(4)	Eu(1)−O(7)	2.681(4)
Eu(1)−O(4)	2.531(4)	Eu(1)−O(8)	2.682(4)
Eu(1)−O(5)	2.737(13)		
O(1)−Eu(1)−O(2)	70.1(1)	O(4)−Eu(1)−O(6)	73.4(1)
O(1)−Eu(1)−O(3)	81.0(1)	O(5)−Eu(1)−O(6)	61.3(2)
O(2)−Eu(1)−O(3)	132.5(1)	O(5B)−Eu(1)−O(6)	61.9(3)
O(1)−Eu(1)−O(4)	120.0(1)	O(1)−Eu(1)−O(7)	88.3(1)
O(2)−Eu(1)−O(4)	93.9(1)	O(2)−Eu(1)−O(7)	77.4(1)
O(3)−Eu(1)−O(4)	68.8(1)	O(3)−Eu(1)−O(7)	139.7(1)
O(1)−Eu(1)−O(5)	145.8(2)	O(4)−Eu(1)−O(7)	145.8(1)
O(2)−Eu(1)−O(5)	138.8(2)	O(5)−Eu(1)−O(7)	83.5(3)
O(3)−Eu(1)−O(5)	84.1(2)	O(5B)−Eu(1)−O(7)	94.9(7)
O(4)−Eu(1)−O(5)	81.9(3)	O(6)−Eu(1)−O(7)	72.4(1)
O(1)−Eu(1)−O(5B)	150.0(3)	O(1)−Eu(1)−O(8)	78.5(1)
O(2)−Eu(1)−O(5B)	139.7(3)	O(2)−Eu(1)−O(8)	128.9(1)
O(3)−Eu(1)−O(5B)	77.4(5)	O(3)−Eu(1)−O(8)	77.8(1)
O(4)−Eu(1)−O(5B)	70.4(7)	O(4)−Eu(1)−O(8)	137.1(1)
O(5)−Eu(1)−O(5B)	11.9(8)	O(5)−Eu(1)−O(8)	68.3(2)
O(1)−Eu(1)−O(6)	145.9(1)	O(5B)−Eu(1)−O(8)	76.8(6)
O(2)−Eu(1)−O(6)	78.2(1)	O(6)−Eu(1)−O(8)	114.1(1)
O(3)−Eu(1)−O(6)	131.6(1)	O(7)−Eu(1)−O(8)	62.0(1)

minimized during least-squares analysis was $\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ where w^{-1} is defined below. The structures were solved by direct methods (SHELXTL PLUS, PC version); and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with d(C−H) = 0.96 Å and U(iso) = 0.08 Å^2. Experimental details are given in Table 1 and in the supplementary material.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for $(THD)_3Sm(DME)$, **3**

Sm(1)−O(1)	2.375(3)	Sm(1)−O(5)	2.383(4)
Sm(1)−O(2)	2.342(4)	Sm(1)−O(6)	2.370(3)
Sm(1)−O(3)	2.346(3)	Sm(1)−O(7)	2.589(3)
Sm(1)−O(4)	2.323(3)	Sm(1)−O(8)	2.597(3)
O(1)−Sm(1)−O(2)	70.5(1)	O(5)−Sm(1)−O(6)	71.1(1)
O(1)−Sm(1)−O(3)	77.7(1)	O(1)−Sm(1)−O(7)	70.9(1)
O(2)−Sm(1)−O(3)	120.4(1)	O(2)−Sm(1)−O(7)	128.9(1)
O(1)−Sm(1)−O(4)	117.5(1)	O(3)−Sm(1)−O(7)	81.5(1)
O(2)−Sm(1)−O(4)	79.9(1)	O(4)−Sm(1)−O(7)	148.9(1)
O(3)−Sm(1)−O(4)	72.1(1)	O(5)−Sm(1)−O(7)	73.4(1)
O(1)−Sm(1)−O(5)	139.5(1)	O(6)−Sm(1)−O(7)	112.4(1)
O(2)−Sm(1)−O(5)	149.9(1)	O(1)−Sm(1)−O(8)	78.4(1)
O(3)−Sm(1)−O(5)	78.7(1)	O(2)−Sm(1)−O(8)	79.4(1)
O(4)−Sm(1)−O(5)	85.3(1)	O(3)−Sm(1)−O(8)	140.5(1)
O(1)−Sm(1)−O(6)	141.4(1)	O(4)−Sm(1)−O(8)	147.4(1)
O(2)−Sm(1)−O(6)	80.6(1)	O(5)−Sm(1)−O(8)	100.6(1)
O(3)−Sm(1)−O(6)	140.4(1)	O(6)−Sm(1)−O(8)	71.6(1)
O(4)−Sm(1)−O(6)	80.4(1)	O(7)−Sm(1)−O(8)	61.1(1)

Eu(THD)$_2$(DME)$_2$, 1. X-ray quality crystals of **1** were grown at −34 °C from a concentrated THF/DME/toluene mixture. A total of 5022 data were collected on a red prism of approximate dimensions 0.20 × 0.37 × 0.40 mm at 158 K. The diffraction symmetry was 2/m with systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] is therefore uniquely defined. The quantity w^{-1} was defined as $\sigma^2(\lvert F_o\rvert) + 0.0002(\lvert F_o\rvert)^2$. Refinement of the model led to a convergence with R_F = 3.7%, R_{wF} = 4.3% and GOF = 1.91 for 352 variables refined against those 3953 data with $\lvert F_o\rvert > 3.0\sigma(\lvert F_o\rvert)$. A final difference-Fourier map yielded ϱ(max) = 0.69 e Å^{-3}.

Sm(THD)$_3$(DME), 3. X-ray quality crystals of **3** were grown at −34 °C from a concentrated THF/DME/toluene mixture. A total of 5864 data were collected on a colorless prism of approximate dimensions 0.40 × 0.45 × 0.46 mm at 158 K. There were no systematic extinctions nor any diffraction symmetry other than the Friedel condition. The two possible triclinic space groups are the noncentrosymmetric $P1$ [C_1^1; No. 1] or the centrosymmetric $P\bar{1}$ [C_i^1; No. 2]. Refinement of the model using the centrosymmetric space group proved it to be the correct choice. The quantity w^{-1} was defined as $\sigma^2(\lvert F_o\rvert) + 0.0005(\lvert F_o\rvert)^2$. Refinement of the model led to a convergence with R_F = 3.3%, R_{wF} = 5.0% and GOF = 1.99 for 416 variables refined against those 5249 data with $\lvert F_o\rvert > 4.0\sigma(\lvert F_o\rvert)$. A final difference-Fourier map yielded ϱ(max) = 0.94 e Å^{-3}.

Results and Discussion

Synthesis. $EuI_2(THF)_2$ reacts with 2 equiv of K(THD) in THF to form a red oil. Addition of DME allows isolation in high yield of monomeric divalent $(THD)_2Eu(DME)_2$, **1**, as a red-orange solid (eq 1).

$$\mathrm{EuI_2(THF)_2 + 2\,K(THD)} \xrightarrow[\text{2. DME}]{\substack{\text{1. THF}\\ -2\mathrm{KI}}} \underset{\mathbf{1}}{\mathrm{(THD)_2Eu(DME)_2}} \qquad (1)$$

$SmI_2(THF)_2$ reacts analogously with 2 equiv of K(THD) to form dark purple $(THD)_2Sm(DME)_2$, **2**. Attempts to crystallize **2** led to the formation of colorless crystals of trivalent $(THD)_3Sm(DME)$, **3** (eq 2).

$$\mathrm{SmI_2(THF)_2 + 2K(THD)} \xrightarrow[\text{2. DME}]{\substack{\text{1. THF}\\ -2\mathrm{KI}}} \underset{\mathbf{2}}{\mathrm{(THD)_2Sm(DME)_2}}$$

$$2 \xrightarrow[\text{1--2 weeks}]{\substack{\text{DME/THF/toluene}\\ -34\ ^\circ\mathrm{C}}} \underset{\mathbf{3}}{\mathrm{(THD)_3Sm(DME)}} \qquad (2)$$

Conversion of divalent lanthanide complexes, $(ligand)_2Sm$, to the trivalent tris(ligand) species, $(ligand)_3Sm$, is quite common for all but the largest ligands such as C_5Me_5. Hence, SmI_3,[10] $Sm[N(SiMe_3)_2]_3$,[16] and $Sm[C_5H_3(SiMe_3)_2]_3$[17] can all be formed

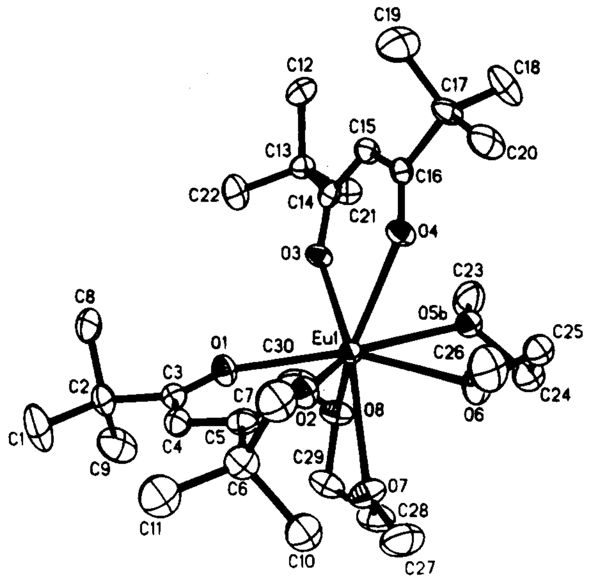

Figure 1. Thermal ellipsoid plot of $(THD)_2Eu(DME)_2$, **1**, with thermal ellipsoids shown at the 50% level.

in this way. The reduction of SmI_3 to SmI_2 by samarium metal is well established[10] and addition of a small amount of samarium metal to solutions of **2** reduces the amount of **3** which forms.

Structure. Compounds **1** and **3** both crystallize as discrete monomeric units in the presence of the chelating solvent DME as shown in Figures 1 and 2. **1** is eight coordinate due to two bidentate β-diketonate ligands and two bidentate DME groups. Three chelating β-diketonates and one DME generate the eight coordinate environment in **3**. Neither dodecahedral nor square antiprismatic[18,19] adequately describe the distorted geometry of donor atoms around the metal centers in **1** and **3**. In contrast, the eight coordinate trivalent europium β-diketonate complexes $(THD)_3Eu(DMF)_2$ (DMF = dimethylformamide),[20] $(THD)_3Eu(py)_2$ (py = pyridine),[21] and $(THD)_3Eu(DMOP)$ (DMOP = 2,9-dimethyl-1,10-phenanthrolene),[22] can be described as square antiprisms.

Although there are no other divalent lanthanide β-diketonates available for comparison, the structural parameters of **1** can be compared with those of the eight coordinate trivalent complexes $(THD)_3Eu(DMF)_2$,[20] $(THD)_3Eu(py)_2$,[21] and $(THD)_3Eu(DMOP)$.[22] The average Eu−O(THD) distance of 2.49(3) Å in **1** is statistically similar to the 2.36(3), 2.35(2), and 2.36(2) Å average Eu−O(THD) distances in $(THD)_3Eu(DMF)_2$,[20] $(THD)_3Eu(py)_2$,[21] and $(THD)_3Eu(DMOP)$,[22] respectively, when the 0.186 Å difference in metallic radii of Eu(II) and Eu(III) is considered.[23] These trivalent Eu−O(THD) values are neartly identical to the average Sm−O(THD) distance of 2.36(2) Å in **3** (the difference in the metallic radii of Eu(III) and Sm(III) is only 0.015 Å[23]). The 2.70(2) Å average Eu−O(DME) distance in **1** is longer than the Eu−O(THD) distance, as expected for neutral donor ligands. This is also seen in **3**, where the average Sm−O(DME) distance is 2.593(4) Å. The analogous bond distances in **1** and **3** are comparable when the difference in metallic radii are taken into consideration.[23]

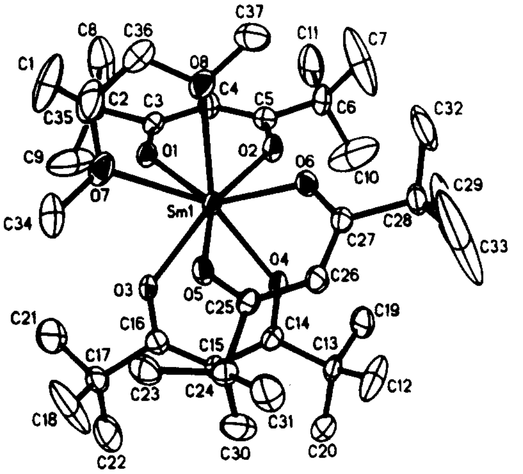

Figure 2. Thermal ellipsoid plot of $(THD)_3Sm(DME)$, **3**, with thermal ellipsoids shown at the 50% level.

Conclusion

The synthesis and structural characterization of $(THD)_2Eu(DME)_2$ shows that tractable divalent lanthanide β-diketonate complexes can be obtained without any unusual synthetic problems. This indicates that this potentially extensive class of complexes is available for exploration and development using the wide variety of β-diketonates known.

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Supplementary Material Available: Tables of crystal data, positional parameters and bond distances and angles (24 pages). Ordering information is given on any current masthead page.

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