[Ca(Thd)$_2$(Tetraen)]: A Monomeric Precursor for Deposition of CaS Thin Films

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[Ca$_3$(thd)$_6$] (thd = 2,2,6,6-tetramethyl-3,5-heptanedionato) dissolved in hexane and in the presence of tetraethylenepentamine (tetraen) crystallizes as a 1:1 [Ca(thd)$_2$(tetraen)] adduct complex in the orthorhombic *Pccn* space group with a = 10.874(2) Å, b = 15.480(3) Å, c = 20.866(4) Å, and Z = 4. The molecule is monomeric with an 8-coordinated calcium atom. The adduct complex volatilized at lower temperature than the nonadducted complex. [Ca(thd)$_2$(tetraen)] can be utilized as a precursor in growth CaS thin films by the atomic layer epitaxy method. The growth rate with [Ca(thd)$_2$(tetraen)] is lower (0.43 Å/cycle) than that with [Ca$_3$(thd)$_6$] (0.50 Å/cycle).

Introduction

CaS as with other alkaline earth metal sulfides has interested material scientists as a host lattice for luminescent materials in both powder and thin film form. CaS thin films doped with di- or trivalent rare-earth ions have widely been studied as potential phosphor materials for color thin-film electroluminescent (TFEL) devices.[1−4] However, the most frequently studied red-emitting CaS:Eu[1,5−10] is today not applied in TFEL devices, but red color is obtained by filtering the yellow-emitting ZnS:Mn.[11]

CaS thin films can be prepared by different methods, viz. sputtering[6,9] and evaporation,[1,2,5,7,8,10,12] but the reports on the use of chemical vapor deposition (CVD)[13−15] and ALE[16−18] method are sparse. In the ALE deposition volatile [Ca$_3$(thd)$_6$] and H_2S have been used as precursors.[16] The more detailed studies on the growth process showed that the decomposition of [Ca$_3$(thd)$_6$] is a problem but stable growth can be achieved if the temperature of the Ca precursor is 180−200 °C and that of reactor 325−400 °C.[17,18]

β-Diketonates and especially thd complexes are the most important precursors of alkaline earth metals needed in chemical vapor deposition of thin films. The thermal instability of these complexes and formation of sparsely volatile oligomers cause problems which are most severe with barium.[19] The partial decomposition of [Sr(thd)$_2$] makes also the ALE processing of SrS thin films difficult.[20,21] Thd complexes have been stabilized by adduct molecules such as amines and polyethers.[22,23] Presuming that the size of the adducting molecule is large enough, the adduct complexes may have the desired monomeric structure. Crystal structures of several adduct complexes of Ba, Sr, and Ca β-diketonates are already known.[23]

In this paper we report the synthesis, thermal behavior, some spectroscopic properties and crystal structure of [Ca(thd)$_2$(tetraen)] complex and describe its behavior as a precursor in ALE growth of CaS thin films.

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Experimental Section

Reagents and Methods. H(thd) (98%) was purchased from Strem Chemicals Inc. $Ca(NO_3)_2 \cdot 4H_2O$ (>98% pure) and *n*-hexane (HPLC grade) were obtained from Merck. Tetraethylenepentamine was purchased from Fluka Chemica and was dried over KOH and distilled before use. Absolute ethanol (>99.6%) was obtained from Oy Alko Ab. Elemental analyses were performed by Geological Survey of Finland (Kuopio). ^1H and ^{13}C NMR spectra in $CDCl_3$ were recorded with a Varian Gemini 2000 instrument at ambient temperature. Chemical shifts were referenced to $SiMe_4$ and are given in ppm. Mass spectra (m/z) were obtained by using a JEOL JMS-SX102 spectrometer operating in an electron impact mode (70 eV). Melting points were measured in air with an Electrothermal melting point apparatus. Thermal analyses were carried out on a Mettler Toledo TA8000 system equipped with a TGA850 thermobalance using a flowing nitrogen atmosphere. The heating rate in thermogravimetry (TG) was 10 °C/min and the sample amounts were between 9 and 10 mg. Isothermal mass-change determinations were performed as follows: The sample (12−22 mg) was heated at a constant temperature (120 °C) for 15 min and the weight loss versus time was recorded. Then the temperature was raised 40 °C and the 15 min isothermal stage was repeated. The measurements were continued up to 280 °C.

Preparation of [$Ca_3(thd)_6$]. The [$Ca_3(thd)_6$] complex was synthesized in aqueous conditions by the previously reported method.[24] The crude product was dried in vacuum for 24 h at 60 °C and purified by sublimation at 6 Pa at a temperature of 210 °C. The white product was collected in glovebox and stored at −20 °C. Colorless crystals, suitable for X-ray analysis, were obtained by dissolving [$Ca_3(thd)_6$] in *n*-hexane and allowing the solvent to evaporate slowly in N_2 atmosphere at room temperature. Yield 88%. Anal. Calcd for $C_{66}H_{114}Ca_3O_{12}$ (1219.86): C, 64.98; H, 9.42. Found: C, 66.9; H, 9.2. Mp 243−245 °C. ^1H NMR ($CDCl_3$) δ 1.06 (s, 36H, $C(CH_3)_3$), 5.66 (s, 2H, CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 28.64 (CH_3), 41.01 ($C(CH_3)_3$), 91.87 (CH), 201.22 (CO). MS (EI, 70 eV) m/z 1035 $[Ca_3(thd)_5]^+$, 812 $[Ca_2(thd)_4]^+$, 629 $[Ca_2(thd)_3]^+$, 349 $[Ca(thd)_2 - C(CH_3)_3]^+$, 223 $[Ca(thd)]^+$, 184 $[H(thd)]^+$, 127 $[H(thd) - C(CH_3)_3]^+$.

Preparation of [$Ca(thd)_2$(tetraen)]. Under a nitrogen atmosphere, 7.00 g (5.74 mmol) of [$Ca_3(thd)_6$] was dissolved in 50 mL of hexane. To this solution was added 4.56 g (24.10 mmol) of tetraethylenepentamine in one portion and the mixture was stirred at ambient temperature for 1 h. Most of the solvent was then removed under reduced pressure, and the remaining solution was left to crystallize at +4 °C. After a few days colorless crystals were collected and dried in vacuum. Yield: 4.64 g (45.2%). Anal. Calcd for $C_{30}H_{61}CaN_5O_4$ (595.93): C, 60.47; H, 10.32; N, 11.75. Found: C, 59.9; H, 9.6; N, 11.0. Mp 110−112 °C. ^1H NMR ($CDCl_3$) δ 1.09 (s, 36H, $C(CH_3)_3$), 2.49 (m, 4H, CH_2), 2.60 (m, 4H, CH_2), 2.73 (m, 4H, CH_2), 2.86 (m, 4H, CH_2), 5.46 (s, 2H, CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 28.85 (CH_3), 40.53 (CH_2-a), 40.65 (CH_2-a), 40.69 ($C(CH_3)_3$), 48.49 (CH_2-b), 48.61 (CH_2-b), 49.59 (CH_2-c), 49.71 (CH_2-c), 51.58 (CH_2-d), 51.70 (CH_2-d), 86.34 (CH), 197.67 (CO). MS (EI, 70 eV) m/z 1035 $[Ca_3(thd)_5]^+$, 812 $[Ca_2(thd)_4]^+$, 629 $[Ca_2(thd)_3]^+$, 412 $[Ca(thd)(tetraen)]^+$, 349 $[Ca(thd)_2 - C(CH_3)_3]^+$, 223 $[Ca(thd)]^+$, 184 $[H(thd)]^+$, 127 $[H(thd) - C(CH_3)_3]^+$, 116, 99, 85, 73, 56, 44.

Single-Crystal X-ray Structure Determination. The X-ray data of [$Ca(thd)_2$(tetraen)] was collected at 153 K using synchrotron radiation (λ = 1.0088 Å) and Fuji image-plates scanned with off-line Fuji 2000 scanner at the beam-line X-7B of the National Synchrotron Light Source at Brookhaven National Laboratory. The complex crystallizes in hexane solution as a monomeric molecule. The crystal selected for X-ray measurements was mounted to the glass fiber using the oil-drop method.[25] The crystal was randomly oriented, and the ω scan used was 5°. Due to the limited dynamic range of the Fuji 2000 scanner another set of images using 10° scans with the beam damped by 24 layers of Al foil were collected to record reliably the strong reflections. The resolution was limited to 0.72 Å due to the size of the image-plates. The resulting 36 5° images and 18 10° images were reduced by DENZO program package,[26,27] resulting in a set of 9936 reflections. The data were corrected for Lorentz and polarization effects. A summary of the crystallographic data, data collection and refinement parameters is given in Table 1. The structure was solved using direct methods, SHELXS,[28] and refined by SHELXL-93 program package.[29] The pictures were produced by SHELXTL PLUS program package.[28]

Table 1. Crystal Data and Structure Refinement for [$Ca(thd)_2$(tetraen)]

empirical formula	$C_{30}H_{61}CaN_5O_4$
formula weight	595.92
temperature	153(2) K
wavelength	1.008 80 Å
crystal system	orthorhombic
space group	P*ccn* (No. 56)
unit-cell dimensions	a = 10.874(2) Å α = 90°
	b = 15.480(3) Å β = 90°
	c = 20.866(4) Å γ = 90°
volume	3512.4(12) $Å^3$
Z	4
density (calculated)	1.127 Mg/m^3
absorption coefficient	1.836 mm^{-1}
$F(000)$	1312
crystal size	0.30 × 0.25 × 0.09 mm^3
θ range for data collection	3.25−44.18°
index ranges	$0 \le h \le 10$, $-20 \le k \le 20$, $-28 \le l \le 28$
reflections collected	9936
independent reflections	3766 [R(int) = 0.1196]
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	3749/51/240
goodness-of-fit on F^2	0.458
final R indexes [$I > 2\sigma(I)$]	$R1$ = 0.0849, $wR2$ = 0.2360
R indexes (all data)	$R1$ = 0.1207, $wR2$ = 0.2821
largest diff peak and hole	0.854 and −0.521 e $Å^{-3}$

tert-Butyl groups, as well as the carbon atoms of the amine ligand refined with large anisotropic temperature factors indicating rotational disorder. In each case disorder models were tested and used where they turned out to be successful. The hydrogen atoms were refined at calculated positions using the riding model. The hydrogen atoms connected to coordinated nitrogens of the amine ligand were not located. The structure was refined with anisotropic temperature factors for the nonhydrogen atoms and isotropic factors for the hydrogen atoms. The temperature factors of the hydrogen atoms were fixed to be 1.5 times the U_{eq} of the parent atoms. The large anisotropic temperature factors in the final refinement clearly indicate the disorder problems, but due to the diffuse electron density around the terminal carbon atoms, disorder models turned out to be quite unstable during the refinement, resulting in chemically unrealistic bond lengths and angles and, even then, quite high anisotropic temperature factors. The amine ligand was refined in two positions with the occupancy of 0.5 fixed for both positions. We believe that the model presented in this article quite successfully describes the structural features of the complex. The fractional coordinates and U_{eq} of the non-hydrogen atoms (including the occupancies of the disordered atoms) are given in Table 2, and selected bond lengths and angles in Table 3.

ALE Film Growth Experiments. The film growth experiments were carried out using a commercial hot-wall flow type F-120 reactor (Microchemistry Ltd., Espoo Finland)[30] operated under a nitrogen pressure of 10 mbar. The films were

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for [Ca(thd)$_2$(tetraen)][a]

atom	*x*	*y*	*z*	U_{eq}
Ca(1)	2500	2500	3877(1)	37(1)
O(1)	2010(3)	1588(2)	4737(1)	64(1)
O(2)	2585(2)	1036(1)	3509(1)	53(1)
C(1)	3066(7)	886(5)	5916(2)	130(2)
C(2)	864(7)	1166(5)	5843(2)	152(3)
C(3)	1474(11)	−304(4)	5696(2)	196(5)
C(4)	1933(6)	590(3)	5581(2)	99(2)
C(5)	2111(4)	813(2)	4862(1)	53(1)
C(6)	2388(4)	175(2)	4414(2)	62(1)
C(7)	2589(3)	312(2)	3768(1)	40(1)
C(8)	2830(3)	−449(2)	3306(2)	48(1)
C(9)	1825(5)	−447(3)	2803(2)	79(1)
C(10)	4036(4)	−262(3)	2939(2)	83(1)
C(11)	2909(8)	−1327(3)	3613(3)	113(2)
N(1A)	460(5)	3019(4)	4315(3)	56(1)
C(2A)	−510(9)	2543(5)	4029(6)	75(3)
C(3A)	−374(9)	2610(6)	3282(5)	70(2)
N(4A)	801(6)	2283(3)	3070(3)	51(1)
C(5A)	1150(11)	2503(5)	2417(4)	69(3)
C(6A)	2386(9)	2224(4)	2265(3)	67(2)
N(1B)	−806(19)	2578(7)	5018(6)	190(8)
C(2B)	−424(10)	3311(7)	4692(4)	84(3)
C(3B)	−631(11)	3191(7)	3968(5)	91(3)
N(4B)	12(9)	2470(5)	3757(4)	65(2)
C(5B)	−285(11)	2202(6)	3111(4)	73(3)
C(6B)	483(8)	2642(5)	2604(4)	55(2)
N(7B)	1749(7)	2367(3)	2699(2)	51(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

deposited on 5 × 5 cm^2 soda lime glass substrates which had been covered with 200 nm thick amorphous Al_2O_3 films. [Ca(thd)$_2$(tetraen)] and [Ca$_3$(thd)$_6$] were evaporated from open boats inside the reactor, and their pulsing on the substrates was accomplished by means of inert gas valving.[30] H_2S (99.999%, Messer Griesheim) was pulsed into the reactor by means of a solenoid valve. Using a needle valve and a mass flow meter, the H_2S flow was adjusted to 10 std cm^3 min^{-1} during a continuous flow.

Film thicknesses and refractive indices were determined by fitting transmittance spectra[31] measured in the wavelength region 370−1100 nm with a Hitachi U-2000 spectrophotometer. Film crystallinity was examined with a Philips MPD 1880 powder X-ray diffractometer using Cu Kα radiation.

Results and Discussion

Synthesis. The complex [Ca(thd)$_2$(tetraen)] was prepared via the reaction of [Ca$_3$(thd)$_6$] with 1.4 times the equimolar amount of tetraethylenepentamine in hexane at ambient temperature. If one equimolar amount of tetraen ligand is used, a white precipitate is formed. This unidentified material is nearly insoluble in common organic solvents and has an inappropriate ^{1}H NMR spectrum. The precipitate can easily be removed by adding more amine which leads to formation of the desired adduct complex. Yield of the [Ca(thd)$_2$(tetraen)] was not very high (45.2%) but it could be increased by concentrating and crystallizing the hexane solution again.

Thermal Analyses. TG and DTG curves of [Ca$_3$(thd)$_6$] and [Ca(thd)$_2$(tetraen)] are shown in Figure 1. Pure [Ca$_3$(thd)$_6$] sublimes completely in a single step as reported earlier.[24,32,33] Under the conditions applied the sublimation takes place in the temperature range 250−370 °C and $T_{50\%} = 345$ °C. The weight loss of [Ca(thd)$_2$(tetraen)] occurs also in a single step. The onset temperature is lower as compared with the parent [Ca$_3$(thd)$_6$], but the sublimation is completed essentially at the same temperature, 370 °C, leaving a minimal residue (0.9%). The 50% weight loss is observed at 323 °C. Sublimation experiments under reduced pressure (8 Pa) show that [Ca(thd)$_2$(tetraen)] sublimes intact almost quantitatively at a temperature of 95 °C. The NMR spectra and TG curves of the sublimed and unsublimed material are identical.

The results of isothermal mass-change determinations are shown in Figure 2, where evaporation rate versus time is represented in a logarithmic scale. The linearity in this plot reflects pure sublimation or vaporization process and the absence of thermal decomposition reactions. As can be seen, [Ca$_3$(thd)$_6$] behaves linearly over the whole temperature range studied. As was already observed in TG, the evaporation of [Ca(thd)$_2$(tetraen)] begins at lower temperature in comparison with [Ca$_3$(thd)$_6$], thus indicating the higher vapor pressure of [Ca(thd)$_2$(tetraen)]. However, at higher temperature [Ca(thd)$_2$(tetraen)] deviates from the linearity implying partial decomposition, most probably the dissociation of the amine ligand. In the evaporation range of an interest for the film growth experiments, [Ca(thd)$_2$(tetraen)] behaves properly.

Mass Spectra. The most intense peak in the mass spectra of both complexes is due to [Ca$_2$(thd)$_3$]$^+$ at *m*/*z* 629, but other oligomeric species, e.g. [Ca$_2$(thd)$_4$]$^+$ at *m*/*z* 812 and [Ca$_3$(thd)$_5$]$^+$ at *m*/*z* 1035, can also be observed. The fragments at *m*/*z* 349 for [Ca(thd)$_2$ − C(CH$_3$)$_3$]$^+$, *m*/*z* 223 for [Ca(thd)]$^+$, and *m*/*z* 127 for [H(thd) − C(CH$_3$)$_3$]$^+$ represent the sequential loss and cleavage of the thd ligand. The molecular ion of the adduct complex is not detected, but a strong peak at *m*/*z* 412 corresponds to the amine containing fragment [Ca(thd)(tetraen)]$^+$. In the low *m*/*z* region there are also present many peaks that are typically observed in the mass spectrum of parent tetraen, e.g., at 44, 56, 73, 85, 99, and 116.[34]

NMR Spectra. The signals observed in the NMR spectra are reported in the experimental section. In the case of pure, as-sublimed [Ca$_3$(thd)$_6$] two characteristic resonances due to the tertiary butyl protons and the proton in the α-carbon are detected in ^{1}H NMR. During prolonged storage in N_2 at −20 °C, two other peaks appear at 1.02 and 5.58 ppm. Hashimoto et al.[35] have investigated chemical stability of CVD source materials and assigned these peaks to free H(thd). Although these peaks are present in the spectrum of [Ca$_3$(thd)$_6$], they have no effect on the adduct syntheses. The ^{1}H NMR spectrum of the adduct complex contains only the two characteristic signals of the thd ligand and the ethylene proton resonances of tetraen. The ^{13}C NMR data for [Ca(thd)$_2$(tetraen)] show only one thd ligand environment but two distinct tetraen environments, indicating two different coordination positions of tetraen.

Single-Crystal X-ray Structures. The [Ca$_3$(thd)$_6$] complex, which we have synthesized in aqueous media

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Ca(thd)_2(tetraen)]^a$

Ca(1)−O(1)	2.345(2)
Ca(1)−O(2)	2.394(2)
Ca(1)−N(4A)	2.521(6)
Ca(1)−N(1A)	2.530(6)
Ca(1)−N(7B)	2.598(5)
Ca(1)−N(4B)	2.717(9)
O(1)−C(5)	1.233(4)
O(2)−C(7)	1.245(3)
C(1)−C(4)	1.489(8)
C(2)−C(4)	1.565(10)
C(3)−C(4)	1.491(6)
C(4)−C(5)	1.552(4)
C(5)−C(6)	1.392(5)
C(6)−C(7)	1.382(4)
C(7)−C(8)	1.544(4)
C(8)−C(11)	1.505(5)
C(8)−C(9)	1.516(6)
C(8)−C(10)	1.546(6)
N(1A)−C(2A)	1.42(1)
C(2A)−C(3A)	1.57(2)
C(3A)−N(4A)	1.44(1)
N(4A)−C(5A)	1.456(10)
C(6A)−C(5A)#1	1.68(2)
N(1B)−C(2B)	1.39(2)
C(2B)−C(3B)	1.54(1)
C(3B)−N(4B)	1.39(1)
N(4B)−C(5B)	1.45(1)
C(5B)−C(6B)	1.51(1)
C(6B)−N(7B)	1.46(1)
O(1)#1−Ca(1)−O(1)	80.2(1)
O(1)#1−Ca(1)−O(2)	143.78(8)
O(1)−Ca(1)−O(2)	71.59(7)
O(1)#1−Ca(1)−O(2)#1	71.59(7)
O(1)−Ca(1)−O(2)#1	143.78(8)
O(2)−Ca(1)−O(2)#1	142.57(10)
O(1)#1−Ca(1)−N(4A)	139.3(2)
O(1)−Ca(1)−N(4A)	105.3(2)
O(2)−Ca(1)−N(4A)	71.8(1)
O(2)#1−Ca(1)−N(4A)	83.3(1)
O(1)#1−Ca(1)−N(4A)#1	105.3(2)
O(1)−Ca(1)−N(4A)#1	139.3(2)
O(2)−Ca(1)−N(4A)#1	83.3(1)
O(2)#1−Ca(1)−N(4A)#1	71.8(1)
N(4A)−Ca(1)−N(4A)#1	96.2(3)
O(1)#1−Ca(1)−N(1A)#1	73.5(2)
O(1)−Ca(1)−N(1A)#1	74.4(2)
O(2)−Ca(1)−N(1A)#1	77.4(2)
O(2)#1−Ca(1)−N(1A)#1	116.8(2)
N(4A)−Ca(1)−N(1A)#1	147.2(2)
N(4A)#1−Ca(1)−N(1A)#1	69.0(2)
O(1)#1−Ca(1)−N(1A)	74.4(2)
O(1)−Ca(1)−N(1A)	73.5(2)
O(2)−Ca(1)−N(1A)	116.8(2)
O(2)#1−Ca(1)−N(1A)	77.4(2)
N(4A)−Ca(1)−N(1A)	69.0(2)
N(4A)#1−Ca(1)−N(1A)	147.2(2)
N(1A)#1−Ca(1)−N(1A)	137.7(3)
O(1)#1−Ca(1)−N(7B)	147.5(1)
O(1)−Ca(1)−N(7B)	127.2(1)
O(2)−Ca(1)−N(7B)	68.5(1)
O(2)#1−Ca(1)−N(7B)	76.1(1)
O(1)#1−Ca(1)−N(7B)#1	127.2(1)
O(1)−Ca(1)−N(7B)#1	147.5(1)
O(2)−Ca(1)−N(7B)#1	76.1(1)
O(2)#1−Ca(1)−N(7B)#1	68.5(1)
N(7B)−Ca(1)−N(7B)#1	37.8(3)
O(1)#1−Ca(1)−N(4B)	107.9(2)
O(1)−Ca(1)−N(4B)	80.4(2)
O(2)−Ca(1)−N(4B)	89.6(2)
O(2)#1−Ca(1)−N(4B)	87.1(2)
N(7B)−Ca(1)−N(4B)	66.3(2)
N(7B)#1−Ca(1)−N(4B)	103.1(2)
O(1)#1−Ca(1)−N(4B)#1	80.4(2)
O(1)−Ca(1)−N(4B)#1	107.9(2)
O(2)−Ca(1)−N(4B)#1	87.1(2)
O(2)#1−Ca(1)−N(4B)#1	89.6(2)
N(7B)−Ca(1)−N(4B)#1	103.1(2)
N(7B)#1−Ca(1)−N(4B)#1	66.3(2)
N(4B)−Ca(1)−N(4B)#1	169.4(3)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + {}^{1}/_{2}, -y + {}^{1}/_{2}, z$.

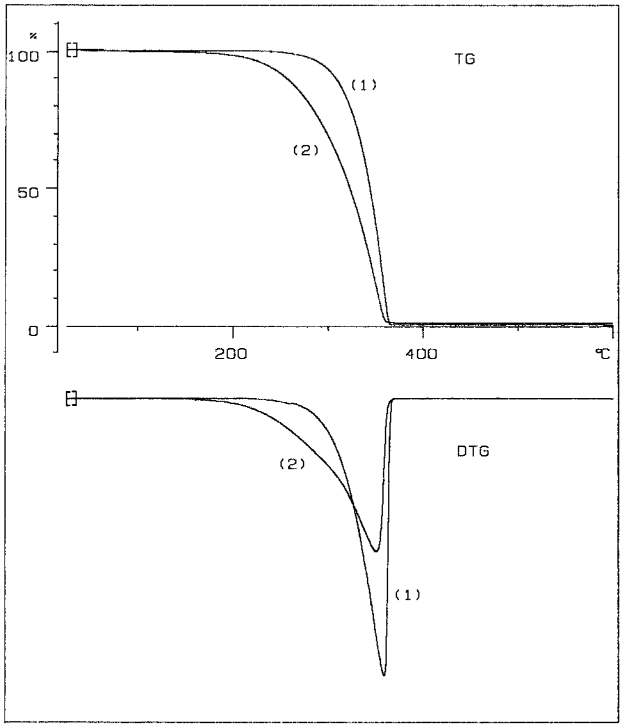

Figure 1. TG and DTG curves of $[Ca_3(thd)_6]$ (**1**) and $[Ca(thd)_2(tetraen)]$ (**2**).

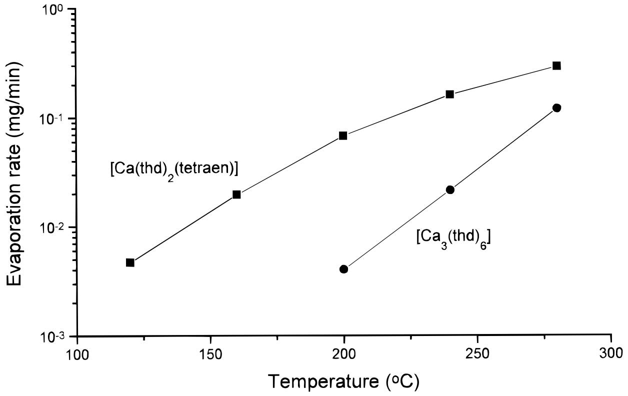

Figure 2. Evaporation rates of $[Ca_3(thd)_6]$ and $[Ca(thd)_2(tetraen)]$ as a function of temperature.

and crystallized from hexane, has the same crystal structure as the complex prepared via the ethoxide-based route by Arunasalam et al.[32] The crystal data at 193 K for the present $[Ca_3(thd)_6]$ is orthorhombic, $Pca2_1$, $a = 20.117(4)$ Å, $b = 19.716(4)$ Å, $c = 18.994$ (4) Å, $V = 7534$ Å^3, $Z = 4$.

In $[Ca(thd)_2(tetraen)]$ the thd ligand coordinates to calcium forming a chelate via O1 and O2 and the tetraen binds to calcium in the meridional plane between the thd ligands (Figure 3). This coordination scheme follows the coordination pattern found in monomeric calcium and barium thd complexes.[36] The amine

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(36) Drake, S. R.; Srewart, S. A. S., Williams, D. J. *Inorg. Chem.* **1993**, *32*, 3227.

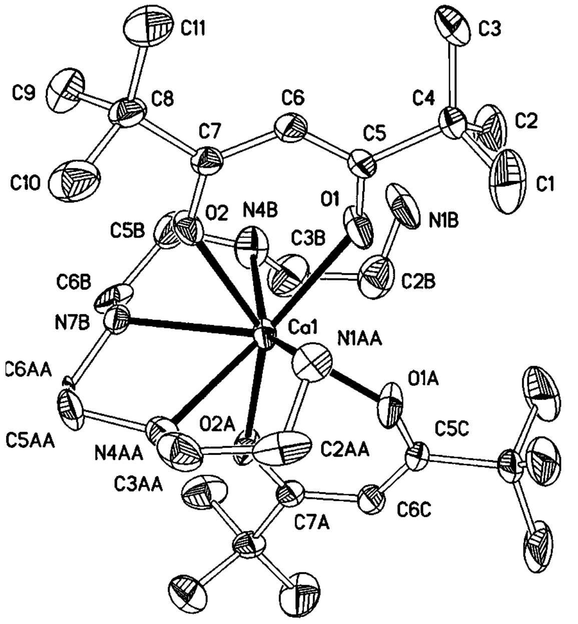

Figure 3. Molecular structure of [Ca(thd)$_2$(tetraen)]. The thermal ellipsoids are drawn at 30% probability level. One conformation of the amine adduct is shown.

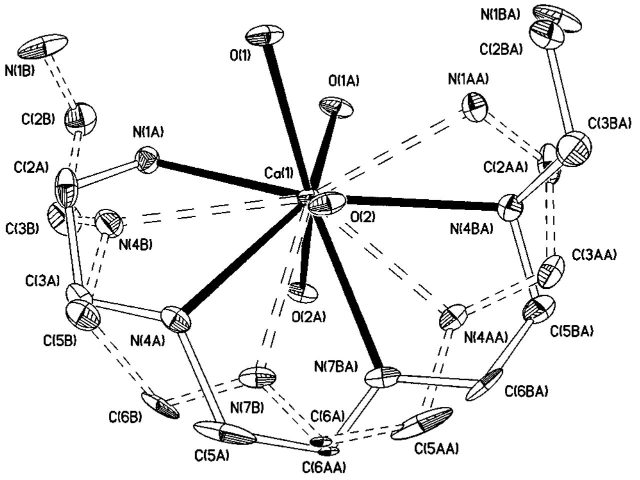

Figure 4. View of the orientation of the two positions of the amine ligand together with the thd oxygens.

ligand is disordered in two positions with half-occupancy (Figure 4). Calcium is located on a 2-fold axis, and thus only half of the molecule had to be determined. The coordination sphere of calcium is a distorted cubic antiprism where two thd molecules coordinate to Ca via four oxygens and the tetraen via four nitrogen atoms. The bond lengths in the calcium coordination sphere can be classified into two groups in which the bond lengths vary from 2.345(2) to 2.394(2) Å for Ca−O and 2.521(6) to 2.717(9) Å for Ca−N distances. Similar pattern can also be seen in monomeric [Ca(thd)$_2$(triglyme)] where the Ca−O$_{\text{thd}}$ bond lengths vary from 2.348(2) to 2.379(2) Å and the Ca−O distances to the neutral triglyme ligand vary from 2.471(3) to 2.594(3) Å.[36] The adduct formation seems to lengthen slightly the Ca−O bonds compared to [Ca$_3$(thd)$_6$], where the values for terminal thd ligands are less than 2.3 Å.[32] A survey of Cambridge Structural Database[37] confirmed that these distances are well within those reported to comparable 8-coordinated calcium complexes with four nitrogen and four oxygen donor atoms, except that the separation to two distinct groups is more pronounced in this complex.[38−40]

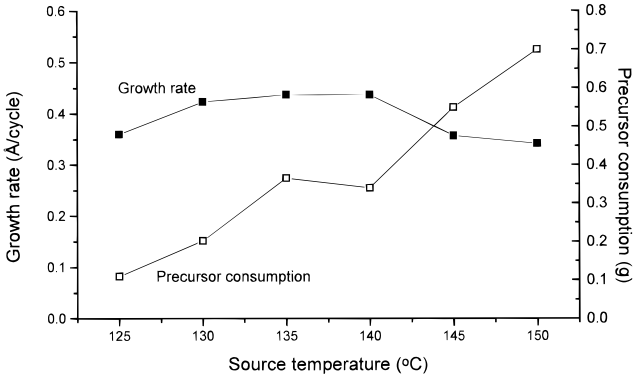

Figure 5. CaS growth rate at 350 °C and the consumption of [Ca(thd)$_2$(tetraen)] as a function of the source temperature. The total number of cycles used was 6000, and the pulse times were 0.6 s for [Ca(thd)$_2$(tetraen)] and 0.2 s for H_2S.

The disordered amine ligand coordinates to Ca through four nitrogen atoms, leaving one terminal amine group uncoordinated (Figure 4). Thus the amine ligand situated in the meridional plane between the thd ligands acts as a belt and bends the thd-ligands toward each other so that the angle O1−Ca1−O1A is 80.2(1)° and O2−Ca1−O2A is 142.6(1)°. These values are typical for alkaline earth metal thd complexes where a bulky ligand fills the coordination sphere of the metal ion.[41−44] The bite angle O1−Ca1−O2, 71.59(7)°, is also typical for chelating thd ligand in an alkaline earth metal complex.[32,45,46]

ALE Growth of CaS: A Comparison between [Ca$_3$(thd)$_6$] and [Ca(thd)$_2$(tetraen)]. The aim of this part of the work was to examine the properties of [Ca(thd)$_2$(tetraen)] as a calcium precursor in ALE growth of CaS, and to compare these properties to those reported previously for [Ca$_3$(thd)$_6$] by Rautanen et al.[18] To ensure the validity of this comparison, the basic experimental conditions, i.e., reactor construction, flow rates of H_2S and nitrogen, and the lengths of precursor pulse and purge periods, were set identical with those used in the previous experiments with [Ca$_3$(thd)$_6$]. In addition, some of the growth experiments with [Ca$_3$(thd)$_6$] were repeated and verified to give results similar to those reported by Rautanen et al.[18]

Figure 5 depicts the effects of [Ca(thd)$_2$(tetraen)] source temperature on precursor consumption and CaS

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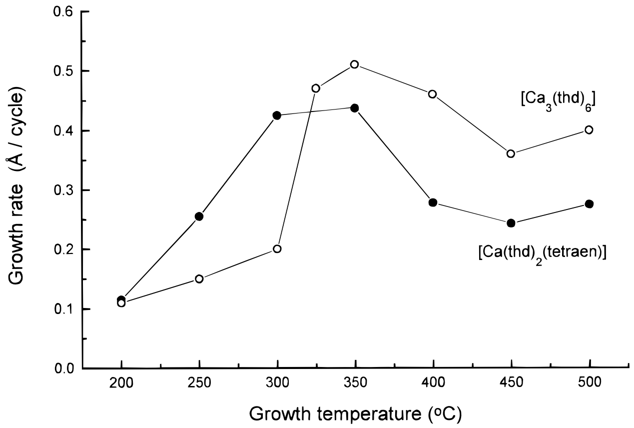

Figure 6. CaS growth rates vs the substrate temperature. The source temperatures were 140 and 190 °C for [Ca(thd)$_2$(tetraen)] and [Ca$_3$(thd)$_6$], respectively. The pulse times were 0.6 s for [Ca(thd)$_2$(tetraen)] or [Ca$_3$(thd)$_6$] and 0.2 s for H$_2$S. The data for [Ca$_3$(thd)$_6$] is from ref 18.

growth rate at a substrate temperature of 350 °C. The consumption of [Ca(thd)$_2$(tetraen)] increases steadily with increasing source temperature. By contrast, the growth rate saturates to a constant maximum level within the source temperature range 130−140 °C. This behavior is in accordance with the basic principle of ALE where the growth rate becomes independent of the precursor flux above a certain limit needed to achieve the full monolayer coverage.[47] The small decrease of the growth rate above a source temperature of 140 °C seems to indicate some kind of aging, most probably decomposition, of [Ca(thd)$_2$(tetraen)] in the heated source during the growth experiment. On these basis, the source temperature range 130−140 °C appears ideal for [Ca(thd)$_2$(tetraen)]. For comparison, the markedly higher optimum source temperature range 180−200 °C was evaluated for [Ca$_3$(thd)$_6$].[18] This difference in source temperatures correlates well with the TG experiments which indicated that the vapor pressure of [Ca(thd)$_2$(tetraen)] is higher than that of [Ca$_3$(thd)$_6$].

A comparison of the CaS growth rates obtained with the two calcium source compounds is shown in Figure 6. With both compounds the optimum temperature region where the growth rate is independent of the temperature, the so-called "ALE-window",[48] is relatively narrow, i.e., 325−400 °C for [Ca$_3$(thd)$_6$] and 300−350 °C for [Ca(thd)$_2$(tetraen)]. Below the lower limits of these regions, the growth rates decrease rapidly with decreasing temperature. This is apparently due to a slowness of the thermally activated surface reactions which are not completed within the given pulse times. Indeed, in the [Ca(thd)$_2$(tetraen)]−H$_2$S process doubling of the pulse times to 0.8 s increased the growth rate at 250 °C to the same level as was obtained at 350 °C already with 0.4 s pulses. By contrast, at 350 °C the growth rate remained unaffected when the pulse times were doubled verifying the completion of the surface reactions at this temperature already with the short pulse times. Therefore, by increasing the pulse times the temperature region for the constant growth rate could be extended toward lower temperatures, but this would cause a marked increase in the overall processing time.

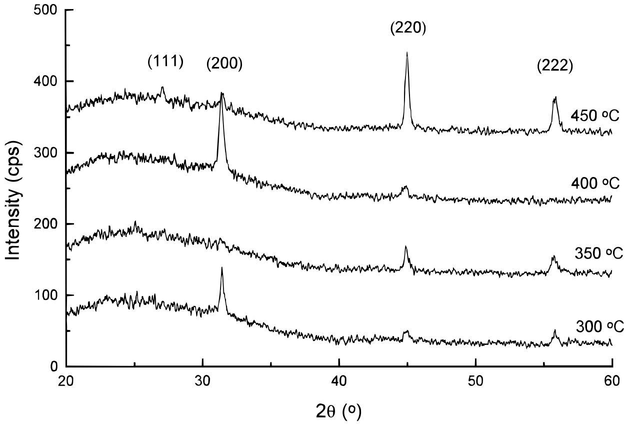

Figure 7. XRD patterns of CaS films deposited from [Ca(thd)$_2$(tetraen)] at different temperatures. All the films have their thicknesses around 250 nm. The peak indexing refers to the cubic CaS structure.[51]

Once the surface reactions are fast enough to become completed within the given pulse times, the growth rates saturate to constant levels. With [Ca(thd)$_2$(tetraen)] this constant level is achieved at a lower temperature than with [Ca$_3$(thd)$_6$] (Figure 6), implying that the surface reactions proceed somewhat faster in the [Ca(thd)$_2$(tetraen)]−H$_2$S process. On the other hand, with [Ca$_3$(thd)$_6$] the constant growth rate is preserved to higher temperatures than with [Ca(thd)$_2$(tetraen)] which exhibits a marked decrease already at 400 °C (Figure 6). It remains an open question whether this decrease is due to a partial desorption of the precursors from the film surface or is due to an increased adsorption site blocking by dissociated thd and tetraen ligands. Above 450 °C the growth rates increase again because of increasing decomposition of the calcium precursors.[17]

The maximum growth rate achieved with [Ca(thd)$_2$(tetraen)] is about 0.43 Å/cycle, while with [Ca$_3$(thd)$_6$] it is higher, about 0.50 Å/cycle. This difference may be related to the additional steric constraints imposed by the tetraen ligands in the chemisorbed [Ca(thd)$_2$(tetraen)] monolayer, which therefore contains a lower density of Ca atoms than the [Ca$_3$(thd)$_6$] monolayer. This explanation requires that the adduct ligand stays intact during the transportation and chemisorption. If this is not the case, the lower growth rate obtained with [Ca(thd)$_2$(tetraen)] may be attributed to the adsorption of tetraen ligands liberated in the decomposition of [Ca(thd)$_2$(tetraen)]. Due to the adsorbed tetraen ligands, the number of adsorption sites available for [Ca(thd)$_2$], or its oligomeric forms, is reduced in comparison with the process employing [Ca$_3$(thd)$_6$] as the calcium source.

XRD studies indicated that the CaS films grown from [Ca(thd)$_2$(tetraen)] have a polycrystalline cubic structure, and the films are rather randomly oriented (Figure 7). While fitting the transmittance spectra, it became obvious that the CaS films consist of two parts: a film bulk with a refractive index of 2.12 ± 0.05 and a thin surface layer for which thicknesses of 25−40 nm and refractive indexes ranging from 1.5 to 1.9 were typically evaluated. The refractive indexes evaluated for the film bulk are comparable to that reported for the bulk material,[49] 2.137, thereby giving an indication of dense film structures. The origin of the heterogeneous surface layer was attributed to a combined effect of surface

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roughness[18] and oxidation of the outermost part of the film.[50]

The CaS films deposited from [$Ca_3(thd)_6$] both in the previous work of Rautanen et al.[18] and in this study exhibited similar XRD patterns and refractive indexes than those presented above for the films obtained from [$Ca(thd)_2$(tetraen)]. Thus, it may be concluded that these two processes result in films with nearly identical structural properties.

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Supporting Information Available: Hydrogen atom coordinates, complete lists of bond lengths and angles, and anisotropic displacement parameters (7 pages); listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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