Strontium β-diketonate complexes with polyamine donor ligands: the synthesis and structural characterization of $[Sr(thd)_2(L)]_n$ ($n = 2$; L = diethylenetriamine, $n = 1$; L = triethylenetetramine, tetraethylenepentamine and tris(2-aminoethyl)amine) complex

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Abstract

Four novel $[Sr(thd)_2(L)]_n$ ($n = 2$; L = diethylenetriamine (**I**), $n = 1$; L = triethylenetetramine (**II**), tetraethylenepentamine (**III**), and tris(2-aminoethyl)amine (**IV**)) complexes were synthesized by the reaction of $Sr(thd)_2$ with corresponding polyamines in THF and characterized by FTIR, ^{1}H NMR and single-crystal X-ray crystallography. Complex **I** exists as a dimmer in the solid state in which two strontium atoms are bridged by two thd ligands. Complexes **II** and **III** exist as monomers in the solid state and in both complexes, the polyamine ligands are coordinated to the central strontium atom in a meridional fashion, with the two thd ligands on opposite sides of the neutral ligand plane. Complex **IV** also exist as a monomer in the solid state. In this molecule, strontium atom is eight-coordinate with all of the nitrogens of the amine ligand and all oxygens of the thd ligand binding to the metal atom. The amine ligand is coordinated to one side of the metal atom and resulting in a *cis*-relationship. Thermogravimetric analysis shows that complexes **I**, **II**, **III** and **IV** are sufficiently volatile and sublimed without residue. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

There has been a continuing interest in the synthesis of alkaline earth metal β-diketonate complexes (particularly Ca, Sr and Ba), because they have been used as promising metal organic chemical vapor deposition (MOCVD) precursors for perovskite metal oxides and ceramic superconductors [1,2]. A useful MOCVD precursor must not only have appropriate reactivity for the desired film growth process but also low volatility and stable vapor pressure characteristics [3]. Monomeric complexes are expected to exhibit an enhanced volatil-ity in comparison to oligomeric complexes because of minimizing intermolecular solid-state interactions and connectivities. Heavier alkaline earth metal bis(β-diketonate) complexes usually exist as oligomeric species ($Ca_3(thd)_6$ [4], $Sr_3(thd)_6(H–thd)$ [5], and $Ba_4(thd)_8$ [6]) (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate) in the solid state. They have relatively low volatility and undergo severe deterioration during storage. They have also unstable vapor pressure as a result of tendency to oligomerize. The main reason for these problems is, among other factors, the large size of the heavier Group II metal ions. To circumvent this problem, recent research interests have been focused on the synthesis of coordinatively saturated Group II metal precursors by introducing ancillary Lewis base ligands. For example, polyether adducts of strontium and bar-

ium complexes, Sr(Ph$_2$acac)$_2$(tetraglyme) [7], Sr(thd)$_2$-(tetraglyme) [7], Ba(thd)$_2$(triglyme) [8], Ba(thd)$_2$-(tetraglyme) [7] are reported. Although these adduct complexes exist as monomeric, exhibiting higher vapor pressure than those of [M(thd)$_2$]$_n$ complexes, the low Lewis acidity of barium and strontium ions weaken the bonding of the adducted polyether chain resulting in dissociation of polyether ligands upon attempted sublimation of the solid and thus have unstable vapor pressure [7,9]. Another approach to improve the volatility and vapor pressure stability of precursors is the introduction of fluorinated β-diketonate ligands [10–13]. However, in many cases, the use of fluorinated β-diketonates necessitates the addition of water vapor as a reactant gas to prevent the formation of undesirable metal fluorides [14,15]. Polyamine adducts of strontium and barium complexes, Sr(hfac)$_2$(bpy)$_2$ [16](hfac = 1,1,1,5,5,5 - hexafluoro - 2,4 - pentanedionate, bpy = 2,2′-dipyridyl), Ba(hfac)$_2$(Phen)$_2$ [17](Phen = o-phenanthroline), Ba(thd)$_2$(pmdt) (pmdt = 1,1,4,7,7-pentamethyldiethylenetriamine) [18], Ba(thd)$_2$(hmtt) (hmtt = 1,1,4,7,10,10 - hexamethyltriethylenetetramine) [18], [Ba(thd)$_2$(diethylenetriamine)]$_2$ [19], [Ba(thd)$_2$-(triethylenetetramine)]$_2$ [19] and [Ba(tfa)$_2$(hmtt)](tfa = 1,1,1,-trifluoro-2,4,-pentanedionate) [20], [Ba(thd)$_2$-(pmdt)](pmdt = pentamethyldiethylenetriamine) [20] [Ba(thd)$_2$(hmtt)](hmtt = hexamethyltriethyleneteramine) [21] have also been reported recently and proven to be effective in reducing molecular aggregation through the coordinative saturation. Because of the increased basicity of amines compared to ethers, it is expected that nitrogen-donor ligands make stronger bonds with metal than analogous oxygen-donor ligands. In this respect, when the polyamines were introduced as neutral ligands to the metal diketonates, it was expected that precursors would exhibit more stable thermal behavior than polyether adducts and simple monodentate Lewis base adducts.

In this article, we report the synthesis and characterization of [Sr(thd)$_2$(L)]$_n$ ($n = 2$; L = diethylenetriamine, $n = 1$; L = triethylenetetramine, tetraethylenepentamine, and tris(2-aminoethyl)amine) complexes which can be used as potential MOCVD precursors for ferroelectric BST((Ba,Sr)TiO$_3$) thin films.

2. Experimental

All manipulations were performed using standard Schlenk line techniques and under dinitrogen atmosphere. Tetrahydrofuran (THF) was distilled after being refluxed with sodium/benzophenone. Acetonitrile, n-pentane, n-hexane were distilled after being refluxed over CaH$_2$ before use. Diethylenetriamine, triethylenetetramine, and tetraethylenepentamine (Aldrich) were

used as received. [Sr(thd)$_2$]$_n$ was synthesized from strontium metal and Hthd in anhydrous THF.

2.1. [Sr(thd)$_2$(diethylenetriamine)]$_2$ (I)

A 250-ml Schlenk flask was charged with Sr(thd)$_2$ (6.61 mmol, 3 g) and a stirring bar. To this flask 100 ml of THF was added via cannula and then diethylenetriamine (6.66 mmol, 0.72 ml) was injected slowly by syringe while stirring at an ambient temperature. The reaction mixture was stirred for a further 4 h and then filtered through a fine porosity funnel. The solvent was removed by vacuum, 30 ml of acetonitrile was then added to the resulting oily crude product, and the solution was stirred for 10 min. Finally white powders were isolated by filtration and dried under vacuum. Yield: 85%. Colorless crystals for single-crystal X-ray structural determination were grown from hot n-hexane solutions. M.p. 128–135°C. Calc. for C$_{52}$H$_{102}$N$_6$O$_8$Sr$_2$: C, 56.03; H, 9.22; N, 7.54. Found: C, 56.20; H, 9.27; N, 7.58%. FTIR: v(NH$_2$,NH); 3386, 3340, 3293 cm^{-1}, v(C=O); 1596 cm^{-1}. ^{1}H NMR (benzene-d_6): δ (CH in thd ligand); 5.81 (s,1H), δ (CH$_3$ in thd ligand); 1.31 (s,18H), δ (CH$_2$ in amine ligand); 2.37 (br,2H), 2.22 (br,2H).

2.2. [Sr(thd)$_2$(triethylenetetramine)] (II)

A 250-ml Schlenk flask was charged with Sr(thd)2 (6.61 mmol, 3 g) and a stirring bar. To this flask 100 ml of THF was added via cannula and then triethylenetetramine (6.71 mmol, 1.00 ml) was injected slowly by syringe while stirring at an ambient temperature. The reaction mixture was stirred for a further 12 h and filtered through a fine porosity funnel. The solvent was removed by vacuum, 30 ml of acetonitrile was then added to the resulting oily crude products and stirred for 10 min. Finally white powders were isolated by filtration and dried under vacuum. Yield: 90%. Colorless crystals for single-crystal X-ray structural determination were grown from hot n-hexane solutions. M.p. 100–106°C. Calc. for C$_{28}$H$_{56}$N$_4$O$_4$Sr: C, 56.01; H, 9.40; N, 9.33. Found: C, 56.25; H, 9.78; N, 9.70%. FTIR: v(NH$_2$,NH); 3382, 3359, 3281, 3316 cm^{-1}, δ (C=O); 1596 cm^{-1}. ^{1}H NMR (benzene-d_6): δ (CH in thd ligand); 5.82 (s,1H), δ (CH$_3$ in thd ligand); 1.34 (s,18H), δ (CH$_2$ in amine ligand); 2.45 (d,2H), 2.22 (br,4H).

2.3. [Sr(thd)$_2$(tetraethylenepentamine)] (III)

A 250-ml Schlenk flask was charged with Sr(thd)$_2$ (6.61 mmol, 3 g) and a stirring bar. To this flask 100 ml of THF was added via cannula and then tetraethylenepentamine (6.64 mmol, 1.26 ml) was injected slowly by syringe stirring at ambient temperature. The reaction mixture was stirred for a further 12 h and filtered

through a fine porosity funnel. The solvent was removed by vacuum, 30 ml of acetonitrile was then added to the resulting oily crude products and then stirred for 10 min. Finally white powders were isolated by filtration and dried under vacuum. Yield: 85%. Colorless crystals for single-crystal X-ray structural determination were grown from hot *n*-hexane solutions. M.p. 84–90°C. Calc. for $C_{30}H_{61}N_5O_4Sr$: C, 56.00; H, 9.56; N, 10.88. Found: C, 56.12; H, 9.86; N, 10.73%. FTIR: $v(NH_2,NH)$; 3394, 3332, 3281 cm^{-1}, $v(C=O)$; 1596 cm^{-1}. ^{1}H NMR (benzene-d_6): δ (CH in thd ligand); 5.74 (*s*,1H), δ (CH$_3$ in thd ligand); 1.31 (*s*,18H), δ (CH$_2$ in amine ligand); 2.66 (*d*,2H), 2.46 (*d*,4H), 2.22 (br,2H).

2.4. [Sr(thd)$_2$(tris(2-aminoethyl)amine)] (IV)

A 250-ml Schlenk flask was charged with Sr(thd)$_2$ (6.61 mmol, 3 g) and a stirring bar. To this flask 100 ml of THF was added via cannula and then tris(2-aminoethyl)amine (6.68 mmol, 1.00 ml) was injected slowly by syringe stirring at an ambient temperature. The reaction mixture was stirred for a further 12 h and filtered through fine porosity funnel. The solvent was removed by vacuum, 30 ml of acetonitrile was then added to the resulting oily crude products and stirred for 10 min. Finally white powders were isolated by filtration and dried under vacuum. Yield: 85%. Colorless crystals for single-crystal X-ray structural determination were grown from hot *n*-hexane solutions. M.p. 76–84°C. Calc. for $C_{24}H_{56}N_4O_4Sr$: C, 56.01; H, 9.40; N, 9.33. Found: C, 56.12; H, 9.34; N, 9.27%. FTIR: $v(NH_2,NH)$; 3370, 3332 cm^{-1}, $v(C=O)$; 1596 cm^{-1}. ^{1}H

NMR (benzene-d_6): δ (CH in thd ligand); 5.80 (*s*,1H), δ (CH$_3$ in thd ligand); 1.35 (*s*,18H), δ (CH$_2$ in amine ligand); 2.29 (*d*,3H), 1.93 (*d*,3H).

2.5. X-ray crystallography

Single crystals of complexes **I**, **II**, **III** and **IV** were obtained directly from saturated *n*-hexane solutions. All of the crystals were subsequently mounted into glass capillary under N$_2$ atmosphere and then sealed. A summary of the X-ray diffraction data is presented in Table 1. The diffraction data was collected at an ambient temperature on Bruker P4 four circle diffractometer using Mo–K$_\alpha$ radiation. The intensity data was collected using a θ–2θ step scan technique and for all data sets the condition of the crystal was monitored by measuring two standard reflections. The solutions of structures **I**, **II**, **III** and **IV** were carried out by a combination of heavy atom Patterson techniques, direct methods, and Fourier techniques. The refinements of the structures by full-matrix-least-squares methods were based on 9051 unique reflections ($2\theta = 45$, $I > 2\sigma$) for **I**, 8485 unique reflections ($2\theta = 45$, $I > 2\sigma$) for **II**, 2455 unique reflections ($2\theta = 45$, $I > 2\sigma$) for **III**, and 2283 unique reflections ($2\theta = 45$, $I > 2\sigma$) for **IV**. Anisotropic temperature factors were used for all non-hydrogen atoms in **I**, **II**, **III**, and **IV**. At the current stage of refinement on 779 parameters for **I**, 715 parameters for **II**, 212 for **III**, and 206 for **IV** with all atoms present in the asymmetric units, $R = 0.0693$, $R_w = 0.1612$ for **I**, $R = 0.0700$, $R_w = 0.1755$ for **II**, $R = 0.0559$, $R_w = 0.1448$ for **III**, and $R = 0.0813$, $R_w = 0.2088$ for **IV**.

Table 1
Crystallographic data for [Sr(thd)$_2$(diethylenetriamine)]$_2$ (**I**), [Sr(thd)$_2$(triethylenetetramine)] (**II**), [Sr(thd)$_2$(tetraethylenepentamine)] (**III**) and [Sr(thd)$_2$(tris(2-aminoethyl)amine)](**IV**)

	I	II	III	IV
Formula	$Sr_2N_6O_8C_{52}H_{102}O_2$	$SrN_4O_4C_{28}H_{56}$	$SrN_5O_4C_{30}H_{61}$	$SrN_4O_4C_{24}H_{56}$
Formula weight	1114.64	600.39	643.36	552.3
Crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1/c$ (No.14)	$P2_1/c$ (No.14)	$Pccn$ (No.56)	$Pnma$ (No.62)
a (Å)	20.528(3)	11.411(4)	11.437(2)	12.178(2)
b (Å)	12.106(2)	16.164(2)	15.868(3)	25.712(5)
c (Å)	26.638(5)	38.508(6)	20.917(6)	11.060(2)
α (°)	90	90	90	90
β (°)	95.06(1)	94.66(2)	90	90
γ (°)	90	90	90	90
Z	4	8	4	4
V (Å)^3	6594(2)	7079(3)	3796(2)	3463.1(11)
T (°C)	20	20	20	20
λ (Å)	0.71073	0.71073	0.71073	0.71073
ρ_{calc} (g cm^{-3})	1.123	1.127	1.124	1.163
μ (cm^{-1})	1.664	1.556	1.455	1.590
R [a] ($I > 2\sigma(I)$)	0.0693	0.0700	0.0559	0.0813
R_w [b] ($I > 2\sigma(I)$)	0.1612	0.1755	0.1448	0.2088

[a] $R = \Sigma ||F_o| - |F_c||/|F_o|$.
[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|^2)]^{1/2}$, where $w = 1/\sigma^2|F_o|)$.

2.6. Other physical measurements

^{1}H NMR spectra (300 MHz) were obtained with Varian Gemini 300 spectrometer. Infrared spectra were measured with a Nicolet Magna-IR 760 spectrometer. CHN analyses were obtained with Thermoquest EA-1110 CHNS analyzer. A controlled thermal analysis of the complexes was investigated using a Perkin–Elmer TGA7 thermogravimetric analyzer, connected to a DECpc personal computer via a TAC 7/DX thermal analysis instrument controller. The weight of the samples investigated was between 6 and 8 mg. The measurements were performed in alumina crucibles under an atmosphere of flowing dry nitrogen gas (25 cm^3 min^{-1}), using heating rates of 5°C min^{-1}.

3. Results and discussion

3.1. Synthesis

The large ionic radius of barium and strontium metal ions (1.18 Å (Ba^{2+}) and 1.35 Å (Sr^{2+}) for C.N. = 6) render coordinatively unsaturation to their complex with average size ligands [22]. Therefore these metal ions will display typically high coordination numbers and their compounds often spontaneously oligomerize. The barium and strontium β-diketonate complexes M(thd)$_2$ exist as tetramer and trimer, respectively, and are highly sensitive to moisture. We have investigated the reaction of the homoleptic M(thd)$_2$ (M = Ba and Sr) complexes with chelating N-donor lewis base ligands. Our previous studies [19] reveal that polyamine ligands can efficiently saturate the coordination sphere of the barium cation and reduce the molecular aggregation. We have investigated the reaction of the homoleptic Sr(thd)$_2$ complexes with the chelating N-donor lewis base ligands. The strontium bis(diketonate) with polyamine adduct complexes [Sr(thd)$_2$(L)]$_n$ ($n = 2$; L = diethylenetriamine (**I**), $n = 1$; L = triethylenetetramine (**II**), tetraethylenepentamine (**III**), and tris(2-aminoethyl)amine (**IV**)) can be obtained from the reaction shown in Scheme 1. The reaction of Sr(thd)$_2$ with one equivalent of polyamines in THF solution proceeds
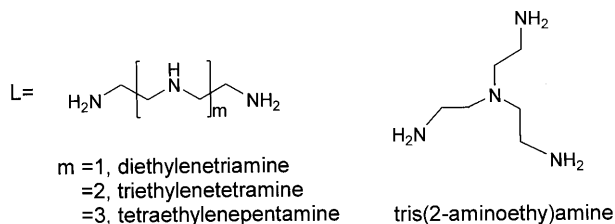
readily at an ambient temperature, under N$_2$ atmosphere, to give a pale yellow solution. The crude white products were purified by recrystalization in *n*-hexane solution and the slightly excess polyamine can be removed easily by washing with acetonitrile. All of the complexes were obtained as colorless crystals in an excellent yield on the crystallization from saturated hot *n*-hexane solution.

The complexes **I**, **II**, **III** and **IV** are highly soluble in non-polar hydrocarbon solvents such as *n*-pentane, *n*-hexane and in polar solvents like diethylether, THF and toluene but insoluble in CH$_3$CN. If 2 equivalents of polyamines are used in the preparation of **I**, **II**, **III**, and **IV** then generally oily products result. Also, all of the complexes **I**, **II**, **III** and **IV** are readily dissolved in small amounts of polyamines. This indicates that the complexes are highly soluble in an excess of the Lewis base, presumably forming more highly ligated complexes. When the commercially available hydrated complex Sr(thd)$_2$·H$_2$O was used as starting materials, the yield was very low and unidentified insoluble powders in hydrocarbon solvents were precipitated. All complexes are relatively stable in air and moisture. The melting points of **I**, **II** and **III** are 128–135, 100–106, 84–90, and 76–84°C respectively, which are significantly lower than that of Sr(thd)$_2$ (200–203°C).

3.2. Spectroscopic data

All of the complexes were characterized by IR, NMR, and elemental analysis. The infrared spectrum of **I**, **II**, **III**, and **IV** exhibit the characteristic N–H stretching vibrational peaks from the amine ligand in the region 3200–3400 cm^{-1}. Also all of the complexes show strong absorption bands at 1596 cm^{-1} due to the C=O stretching vibrational peaks from thd ligands. ^{1}H NMR spectra of all four complexes in C$_6$D$_6$ show only a characteristic signal for one type of thd and polyamine ligand environment at room temperature. The ethylene proton resonances of coordinated polyamines are broad and unresolved sharply in all four spectra. The integration ratio of thd to polyamine ligand was observed to be 2:1 which indicate all four complexes have Sr(thd)$_2$(L) formula in solution state which are in agreement with elemental analyses. Analytical and spectroscopic data for all four complexes are in accordance with the structures determined by X-ray crystallography, discussed in detail in the following section.

3.3. Single-crystal X-ray structures

To investigate the structure in the solid state, X-ray single–crystal structural studies were undertaken for all four complexes, which reveal that **I** exists as a dinuclear complex, [Sr(thd)$_2$(diethylenetriamine)]$_2$. On the other

[Sr(thd)$_2$]$_n$ + nL ⟶ [Sr(thd)$_2$(L)]$_n$

L=

m =1, diethylenetriamine
  =2, triethylenetetramine
  =3, tetraethylenepentamine

tris(2-aminoethy)amine

Scheme 1.

hand, **II**, **III**, and **IV** exist as mononuclear complexes, [Sr(thd)$_2$(triethylenetetramine)], [Sr(thd)$_2$(tetraethylene-pentamine)], [Sr(thd)$_2$(tris(2-aminoethyl)amine)], respectively. The selected bond distances and angles of complex **I**, **II**, **III**, and **IV** are presented in Tables 2 and 3.

3.4. [Sr(thd)$_2$(diethylenetriamine)]$_2$ (**I**)

The single-crystal X-ray structure of complex **I** is shown in Fig. 1. In complex **I**, each strontium metal is a eight coordinate, with a distorted propellane fashion, where a terminal amine ligand and three thd ligands are coordinated to strontium metal. The two strontium atoms are bridged by two thd ligands, in which two amine ligands and two terminal thd ligands are coordinated as *trans* fashion. Each strontium atom in complex **I** is coordinated with three nitrogen atoms (Sr–N average 2.77 Å) from diethylenetriamine and five oxygen atoms, two from the terminal thd ligand and three from the bridging thd ligand. The distances in bridging Sr–O$_{thd}$ (average 2.634 Å) are significantly longer than those in terminal chelating ones (average 2.521 Å) as expected. The O–Sr–O chelate angles for the terminal thd ligands are 67.6(3)° (O(1)–Sr(1)–O(2)) and 69.6(3)°(O(5)–Sr(1)–O(6)). These values are larger than those observed in bridging thd ligands (66.7(2)° for O(3)–Sr(1)–O(4) and 66.2° for O(7)–Sr(1)–O(8)). The N–Sr–N angles for amine ligands are nearly identical and are in the range from 62.4(5)°–63.6(5)°.

3.5. [Sr(thd)$_2$(triethylenetetramine)] (**II**)

For complex **II**, there are two molecules in the asymmetric unit that are nearly identical within the precision

of experiment. In Fig. 2, their structures and relative positioning were illustrated. In each molecule, strontium atom is eight coordinate with all of the nitrogens of the triethylenetetramine ligand and all oxygens of the thd ligand binding to the metal atom. Both Sr(1) and Sr(2) are coordinated in an meridional fashion by triethylenetetramine ligands, with two bidentate thd ligands on opposite sides of the amine ligand mean plane. This coordination environment is similar to the coordination pattern found in eight coordinated Ba and Ca triglyme adducts, Ca(thd)$_2$(triglyme) and Ba(thd)$_2$-(triglyme) complexes [8], but is different from those in Sr(hfac)$_2$(bpy)$_2$ [16], where the central Sr atom is eight coordinated with two hfac moieties on one side and the two bpy ligands on the other side. The Sr–O thd distances are in the range from 2.480(7)–2.555(6) Å (average 2.513 Å) for Sr(1) and from 2.458(6)–2.511(6) Å (average 2.491 Å) for Sr(2) which are slightly shorter than those in complex **I**. The Sr–N distances (average 2.75 Å in each molecule) are slightly shorter than those of complex **I**. The O–Sr–O chelate angles for the terminal thd ligands in both molecules are little different (average 67.95 (O–Sr(1)–O) and 68.8°(O–Sr(2)–O) and are comparable for those in complex **I**. The N–Sr–N angles for amine ligands are nearly identical and are in the range from 63.1(4)–64.6(3)°.

3.6. [Sr(thd)$_2$(tetraethylenepentamine)] (**III**)

The single-crystal X-ray structure of complex **III** is shown in Fig. 3. Strontium atom and N(1) atom are located on crystallographic 2-fold axis, and thus half of the molecule had to be determined. Strontium atom is nine coordinate with all of the nitrogens of the tetra-

Table 2
Selected bond lengths (Å) for complexes **I**, **II**, **III** and **IV**

Complex I							
Sr(1)–O(1)	2.505(9)	Sr(2)–O(3)	2.718(8)	Sr(1)–N(1)	2.760(11)	Sr(2)–N(4)	2.751(12)
Sr(1)–O(2)	2.548(9)	Sr(2)–O(5)	2.470(9)	Sr(1)–N(2)	2.74(2)	Sr(2)–N(5)	2.83(2)
Sr(1)–O(3)	2.618(8)	Sr(2)–O(6)	2.515(9)	Sr(1)–N(3)	2.819(11	Sr(2)–N(6)	2.724(12)
Sr(1)–O(4)	2.536(8)	Sr(2)–O(7)	2.616(8)				
Sr(1)–O(7)	2.584(8)	Sr(2)–O(8)	2.554(10)				
Complex II							
Sr(1)–O(1)	2.511(6)	Sr(1)–N(1)	2.774(10)	Sr(2)–O(5)	2.502(6)	Sr(2)–N(5)	2.763(12)
Sr(1)–O(2)	2.505(6)	Sr(1)–N(2)	2.742(10)	Sr(2)–O(6)	2.494(7)	Sr(2)–N(6)	2.749(11)
Sr(1)–O(3)	2.555(6)	Sr(1)–N(3)	2.775(10)	Sr(2)–O(7)	2.511(6)	Sr(2)–N(7)	2.779(12)
Sr(1)–O(4)	2.480(7)	Sr(1)–N(4)	2.723(8)	Sr(2)–O(8)	2.458(6)	Sr(2)–N(8)	2.720(11)
Complex III							
Sr–O(1A)	2.515(4)	Sr–N(1)	2.743(10)	Sr–N(3A)	2.786(7)		
Sr–O(1)	2.515(4)	Sr–N(2)	2.768(11)				
Sr–O(2A)	2.576(4)	Sr–N(2A)	2.768(11)				
Sr–O(2)	2.576(4)	Sr–N(3)	2.786(7)				
Complex IV							
Sr–O(1)	2.656(7)	Sr–N(1)	2.702(13)	Sr–N(3)	2.768(8)		
Sr–O(2)	2.466(7)	Sr–N(2)	2.773(10)				

Table 3
Selected bond angles (°) for complexes **I**, **II**, **III** and **IV**

Complex I

O(1)–Sr(1)–O(4)	87.6(3)	N(2)–Sr(1)–N(1)	62.9(5)	O(6)–Sr(2)–N(6)	73.7(5)
O(1)–Sr(1)–O(2)	67.6(3)	O(1)–Sr(1)–N(3)	135.9(4)	O(8)–Sr(2)–N(6)	143.1(5)
O(4)–Sr(1)–O(2)	144.4(3)	O(4)–Sr(1)–N(3)	136.4(4)	O(7)–Sr(2)–N(6)	84.2(5)
O(1)–Sr(1)–O(7)	114.7(3)	O(2)–Sr(1)–N(3)	72.1(4)	O(3)–Sr(2)–N(6)	74.1(4)
O(4)–Sr(1)–O(7)	79.0(3)	O(7)–Sr(1)–N(3)	80.6(4)	O(5)–Sr(2)–N(4)	79.5(4)
O(2)–Sr(1)–O(7)	88.3(3)	O(3)–Sr(1)–N(3)	72.4(4)	O(6)–Sr(2)–N(4)	72.2(4)
O(1)–Sr(1)–O(3)	147.2(3)	N(2)–Sr(1)–N(3)	62.9(5)	O(8)–Sr(2)–N(4)	67.3(5)
O(4)–Sr(1)–O(3)	66.7(2)	N(1)–Sr(1)–N(3)	118.5(5)	O(7)–Sr(2)–N(4)	117.6(4)
O(2)–Sr(1)–O(3)	144.2(3)	O(5)–Sr(2)–O(6)	69.6(3)	O(3)–Sr(2)–N(4)	162.1(4)
O(7)–Sr(1)–O(3)	81.4(3)	O(5)–Sr(2)–O(8)	81.5(3)	N(6)–Sr(2)–N(4)	112.5(6)
O(1)–Sr(1)–N(2)	88.4(4)	O(6)–Sr(2)–O(8)	133.6(3)	O(5)–Sr(2)–N(5)	141.6(4)
O(4)–Sr(1)–N(2)	133.8(4)	O(5)–Sr(2)–O(7)	129.9(3)	O(6)–Sr(2)–N(5)	93.2(4)
O(2)–Sr(1)–N(2)	73.0(4)	O(6)–Sr(2)–O(7)	157.9(3)	O(8)–Sr(2)–N(5)	87.4(4)
O(7)–Sr(1)–N(2)	142.5(4)	O(8)–Sr(2)–O(7)	66.2(3)	O(7)–Sr(2)–N(5)	76.3(4)
O(3)–Sr(1)–N(2)	94.9(4)	O(5)–Sr(2)–O(3)	84.5(3)	O(3)–Sr(2)–N(5)	132.4(4)
O(1)–Sr(1)–N(1)	67.1(4)	O(6)–Sr(2)–O(3)	94.9(3)	N(6)–Sr(2)–N(5)	63.6(5)
O(4)–Sr(1)–N(1)	73.3(4)	O(8)–Sr(2)–O(3)	118.2(3)	N(4)–Sr(2)–N(5)	62.4(5)
O(2)–Sr(1)–N(1)	115.9(4)	O(7)–Sr(2)–O(3)	79.0(2)	Sr(1)–O(3)–Sr(2)	94.9(3)
O(7)–Sr(1)–N(1)	152.2(3)	O(5)–Sr(2)–N(6)	135.3(5)	Sr(1)–O(7)–Sr(2)	98.2(3)
O(3)–Sr(1)–N(1)	85.5(4)				

Complex II

O(4)–Sr(1)–O(1)	137.3(2)	N(4)–Sr(1)–N(3)	63.3(3)	O(8)–Sr(2)–N(8)	80.3(4)
O(4)–Sr(1)–O(2)	92.7(2)	N(2)–Sr(1)–N(3)	64.6(3)	O(6)–Sr(2)–N(8)	72.4(4)
O(1)–Sr(1)–O(2)	68.2(2)	O(4)–Sr(1)–N(1)	81.0(3)	O(5)–Sr(2)–N(8)	119.2(4)
O(4)–Sr(1)–O(3)	67.7(2)	O(1)–Sr(1)–N(1)	121.4(3)	O(7)–Sr(2)–N(8)	77.2(4)
O(1)–Sr(1)–O(3)	147.3(2)	O(2)–Sr(1)–N(1)	67.9(3)	N(6)–Sr(2)–N(8)	121.8(5)
O(2)–Sr(1)–O(3)	141.8(2)	O(3)–Sr(1)–N(1)	76.5(3)	O(8)–Sr(2)–N(7)	139.0(3)
O(4)–Sr(1)–N(4)	90.3(3)	N(4)–Sr(1)–N(1)	164.5(4)	O(6)–Sr(2)–N(7)	102.8(4)
O(1)–Sr(1)–N(4)	73.5(3)	N(2)–Sr(1)–N(1)	64.1(4)	O(5)–Sr(2)–N(7)	82.6(3)
O(2)–Sr(1)–N(4)	125.7(3)	N(3)–Sr(1)–N(1)	112.6(4)	O(7)–Sr(2)–N(7)	82.6(3)
O(3)–Sr(1)–N(4)	88.3(3)	O(8)–Sr(2)–O(6)	83.4(2)	N(6)–Sr(2)–N(7)	63.2(4)
O(4)–Sr(1)–N(2)	144.2(3)	O(8)–Sr(2)–O(5)	135.0(2)	N(8)–Sr(2)–N(7)	63.9(4)
O(1)–Sr(1)–N(2)	72.9(3)	O(6)–Sr(2)–O(5)	67.6(2)	O(8)–Sr(2)–N(5)	80.0(4)
O(2)–Sr(1)–N(2)	81.7(3)	O(8)–Sr(2)–O(7)	70.0(2)	O(6)–Sr(2)–N(5)	120.5(3)
O(3)–Sr(1)–N(2)	95.3(3)	O(6)–Sr(2)–O(7)	142.4(2)	O(5)–Sr(2)–N(5)	86.0(4)
N(4)–Sr(1)–N(2)	121.6(4)	O(7)–Sr(2)–N(5)	149.2(2)	O(5)–Sr(2)–O(7)	81.3(3)
O(4)–Sr(1)–N(3)	128.4(2)	O(8)–Sr(2)–N(6)	131.3(3)	N(6)–Sr(2)–N(5)	63.1(4)
O(1)–Sr(1)–N(3)	79.5(2)	O(6)–Sr(2)–N(6)	142.0(3)	N(8)–Sr(2)–N(5)	154.8(5)
O(2)–Sr(1)–N(3)	138.9(2)	O(5)–Sr(2)–N(6)	75.4(3)	N(7)–Sr(2)–N(5)	126.3(4)
O(3)–Sr(1)–N(3)	68.0(2)	O(7)–Sr(2)–N(6)	73.9(3)		

Complex III

O(1A)–Sr–O(1)	92.6(2)	N(2A)–Sr–N(3)	153.3(3)	N(1)–Sr–(2A)	64.0(3)
O(2A)–Sr–N(2)	75.6(2)	O(1)–Sr–O(2)	67.26(12)	O(2)–Sr–(3A)	118.9(2)
O(2)–Sr–N(3)	80.4(2)	O(1)–Sr–N(2A)	87.5(3)	O(2A)–Sr–N(1)	70.52(8)
O(1A)–Sr–O(2A)	67.26(12)	O(1A)–Sr–N(3A)	72.3(2)	N(2)–Sr–N(2A)	128.0(5)
O(2)–Sr–N(2)	87.5(2)	O(2A)–Sr–O(2)	141.0(2)	N(1)–Sr–N(3A)	118.3(2)
N(1)–Sr–N(3)	118.3(2)	O(2A)–Sr–(2A)	87.5(2)	O(2)–Sr–N(1)	70.52(8)
O(1)–Sr–O(2A)	147.91(14)	O(1)–Sr–N(3A)	69.4(2)	O(1A)–Sr–N(3)	69.4(2)
N(1)–Sr–N(2)	64.0(3)	O(1A)–Sr–N(1)	133.6(1)	N(2)–Sr–N(3A)	153.3(3)
N(2)–Sr–N(3)	61.5(3)	O(2A)–Sr–N(2A)	75.6(2)	O(1A)–Sr–N(2)	87.5(3)
O(1A)–Sr–O(2)	147.91(14)	O(2A)–Sr–(3A)	80.4(2)	O(1)–Sr–N(3)	72.3(2)
O(1A)–Sr–N(2A)	130.5(3)	O(1)–Sr–N(1)	133.6(1)	N(2A)–Sr–(3A)	61.5(3)

Complex IV

O(2)–Sr–O(1)	66.1(2)	O(1)–Sr–O(1A)	130.5(3)	O(2)–Sr–O(2A)	73.5(3)
N(1)–Sr–N(2)	66.8(3)	N(2)–Sr–N(3)	64.6(2)	N(1)–Sr–N(3)	113.9(4)
N(3)–Sr–N(3A)	81.5(4)				

ethylenepentamine ligand and all oxygens of the thd ligand binding to the metal atom. The amine ligand is observed to be located on a meridional plane, with two bidentate thd ligands lying respectively above and below the plane. Similar coordination fashion was found in those of Ba(thd)$_2$(tetraglyme) [7], Ba(hfa)$_2$(tetraglyme) [25], Ca(hfa)$_2$(tetraglyme) [8] and Ca(thd)$_2$(tetraethylenepentamine) [26] complexes. But in the case of Ca complexes, only four out of five donor atoms in the ancillary ligand are coordinated to the central Ca atom and coordination number is eight in those complexes.
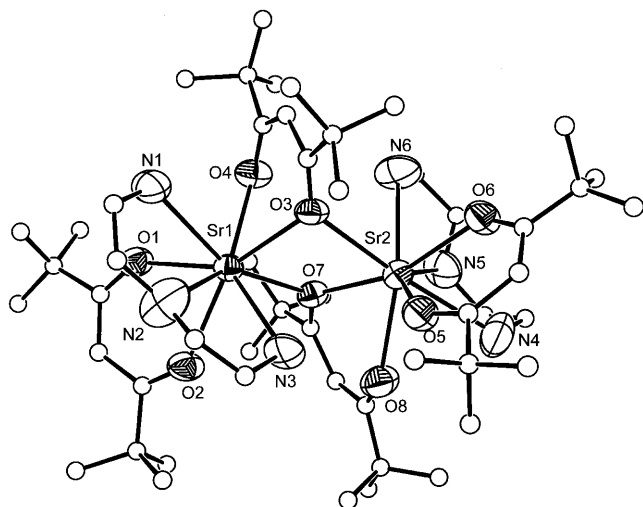
Fig. 1. Molecular structure and labeling of [Sr(thd)$_2$(diethylenetriamine)]$_2$ (**I**). Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces. Hydrogen atoms have been omitted for clarity.
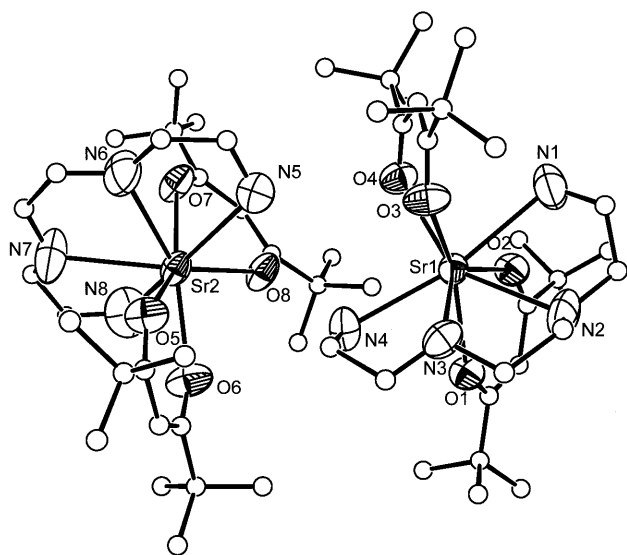
Fig. 2. Molecular structure, labeling and relative positions of the two molecules of [Sr(thd)$_2$(triethylenetetramine)] (**II**). Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces. Hydrogen atoms have been omitted for clarity.
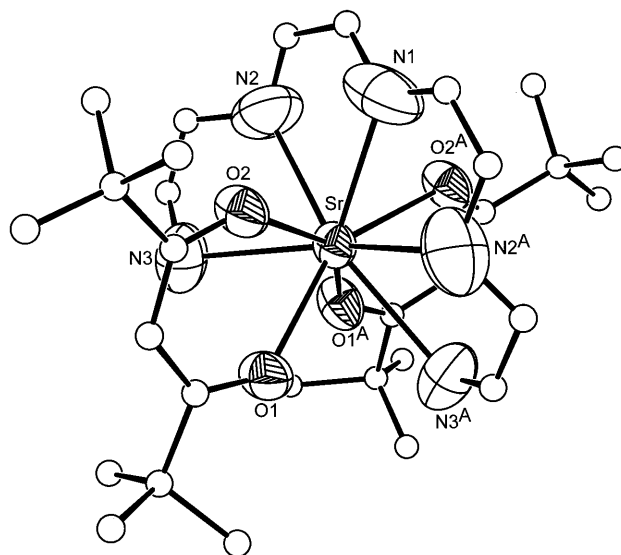

Fig. 3. Molecular structure and labeling of [Sr(thd)$_2$(tetraethylenepentamine)] (**III**). Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces. Hydrogen atoms have been omitted for clarity. Symmetry-generated atoms have the suffix A.
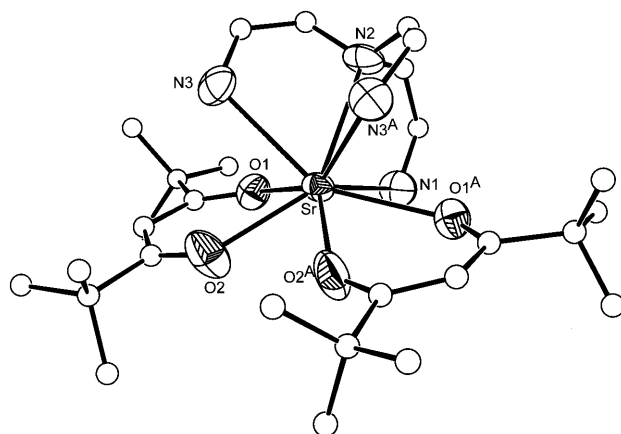

Fig. 4. Molecular structure and labeling of [Sr(thd)$_2$(tris(2-aminoethyl)amine)] (**IV**). Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces. Hydrogen atoms have been omitted for clarity. Symmetry-generated atoms have the suffix A.

This difference between our strontium analogues and other barium analogues may be due to the smaller ionic radius of the Ca cation than those of barium and strontium. The Sr–O thd distances are in the range from 2.515(4)–2.576(4)Å (average 2.546 Å) which are apparently longer than those in complex **I** and **II**. These longer Sr–O distances in complex **III** reflect the strong chelating effect and higher denticity of tetraethylenepentamine ligand. The Sr–N(1) distance (2.720 Å) is significantly shorter than that of Sr–N(2) (2.768 Å) and Sr–N(3)(2.786 Å). The O–Sr–O chelate angles for the thd ligands are 67.26(12)° and the N–Sr–N angles for amine ligands are in the range from 61.5(4)–64.0(3)°.
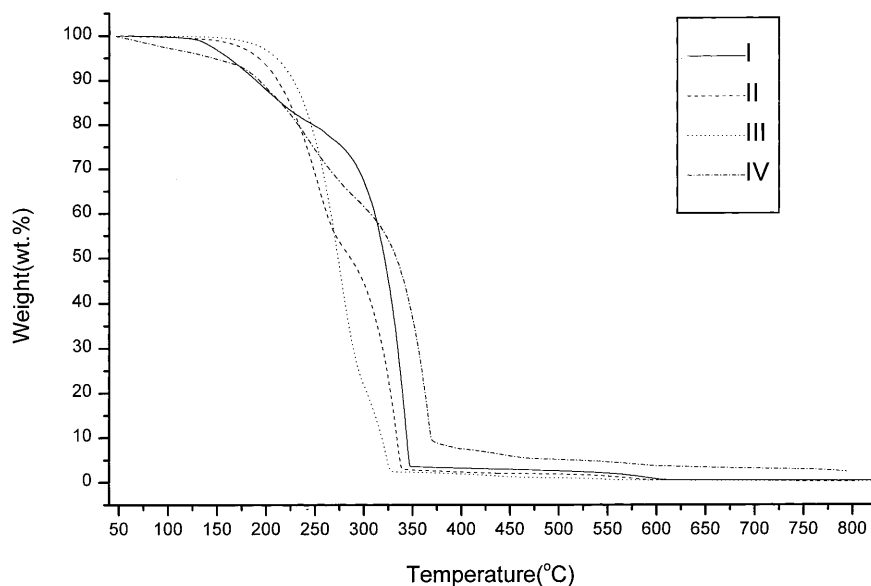
Fig. 5. Thermogravimetric analyses of complexes **I**, **II**, **III** and **IV** under N_2 with a temperature ramp of 5°C min^{-1}.

3.7. [Sr(thd)₂(tris(2–aminoethylene)amine)] ((IV)

The single-crystal X-ray structure of complex **IV** are shown in Fig. 4. The molecule in **IV** occupies a crystallographic mirror plane in which strontium, N(2) and N(3) atoms are located on a mirror plane. In this molecule, strontium atom is eight coordinate with all of the nitrogens of the amine ligand and all oxygens of the thd ligand binding to the metal atom. The amine ligand is coordinated to one side of the metal atom and resulting in a *cis*–relationship of the thd ligands with an O–M–O angle of 66.1(2). This coordination environment is similar to the coordination pattern found in Sr(hfac)₂(bpy)₂ [16], [Ba(hfac)₂(CH₃OCH₂CH₂)₃N] [23], but is different from those in complex **II**, **III** and polyglyme adducts of barium and strontium β-diketonates, where polyamine or polyglyme ligands are coordinated to metal atom in meridional fashion with two β-diketonate moieties being positioned on either side of this plane. The Sr–N distances show different patterns in two molecules.

3.8. Thermal analyses

Thermogravimetric data for complexes **I**, **II**, **III** and **IV** which were collected under an N_2 atmosphere with a 5°C min^{-1} temperature ramp rate are shown in Fig. 4. It is immediately apparent that all complexes are sufficiently volatile and sublime or evaporate without residue. Upon heating under nitrogen, complex **I** and **II** undergo two major steps of weight loss. The first weight loss occurs at ca 100–250°C (ca. 20%) for **I** and ca 150–275°C (ca. 45%) for **II** and this represents the loss of amine ligand in the complexes. A similar result was reported earlier for [Sr(thd)(tetraglyme)] complex [7] in

which the loss of tetraglyme ligand occurs at 150–260°C. The DSC plot for complex **I** and **II** reveals only two endotherms. The first sharp isotherms are attributed to the melting, centered at 134.21°C for **I** and 105.52°C for **II** which are in agreement with a visual observation. The second broad isotherms are centered at 342.39°C for **I** and 359.69°C for **II**, which are presumably due to separation and evaporation of amine ligand. However in complexes **III** and **IV**, there is no evidence for loss of amine ligand. Fig. 4 shows that complex **III** and **IV** sublime and vaporize without decomposition over the temperature range ca. 150–330°C and ca. 100–370°C, respectively. The DSC plot for complex **III** and **IV** reveals only one endotherm centered at 88.29°C for **III** and 70.96°C for **IV** which is attributed to the melting. All four complexes show enhanced thermal stability than those of Sr(thd)₂(H–thd) [24] and Sr(thd)₂(tetraglyme) [7]. In Sr(thd)₂(H–thd) complex, the loss of H–thd occurs below 200°C and followed by sublimation of the remaining [Sr(thd)₂]ₙ between ca. 270–390°C to give a residue of 3.4% Fig. 5.

4. Conclusion

A new class of volatile strontium bis(diketonate) with polyamine adducts has been successfully synthesized and characterized. From the molecular structures determined by single-crystal X-ray analyses, it is possible to explain that the minimum coordination number for saturating strontium cation coordination sphere is 8. In fact, coordinatively unsaturated Sr(thd)₂(diethylenetriamine) (coordination number 7) exist as a dimmer by bridging one of oxygen atom from thd ligand in adja-

cent molecule and thus satisfy coordinative saturation number 8. On the other hand, coordinatively saturated complexes **II**, **III** and **IV** exist as monomer. These complexes, when compared to Sr(thd)$_2$, offer the advantages of air/moisture stability and enhanced thermal stability. Therefore it is expected that these complexes are promising MOCVD precursors for BST thin films.

5. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 145280 for complex **I**, CCDC No. 145281 for complex **II**, CCDC No. 145282 for complex **III** and CCDC No. 145283 for complex **IV**. Copies of this information may be obtained free of charge from The Director, 12 Union road, Cambridge, CB2 1EZ, UK (fax: + 44-1223-336033; e-mail: deposit @ccdc.cam.ac.uk or www: http://www.ccdc.cam. ac.uk).

Acknowledgements

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