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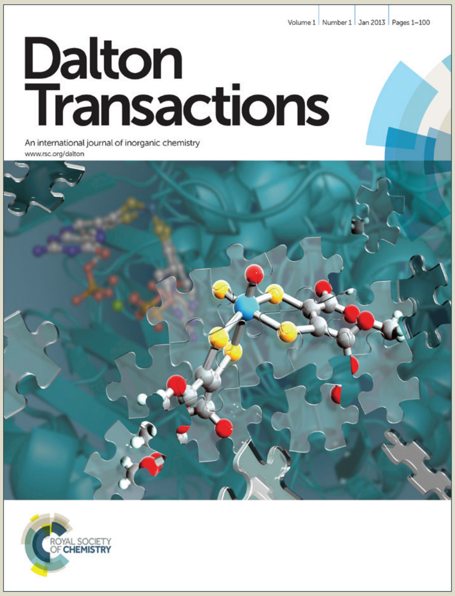

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ARTICLE

Synthesis of New Heteroleptic Strontium Complexes

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A series of heteroleptic strontium complexes (**1**-**9**) using a combination of different aminoalkoxides and 2,2,6,6-tetramethyl-3,5-heptanedionate (tmhd) were prepared to examine the effect of the bulkiness and coordination ability of the aminoalkoxide ligand in these complexes as well as potential strontium precursors. All complexes were characterized by FT-IR, FT-NMR, elemental analyses, and thermo-gravimetric (TG) analyses. The crystal structure analyses of **1**, **2**, **4**, and **5** demonstrate their stability in dimer form and the unwillingness of the strontium atom to form more than six coordination bonds in these complexes. Complex **5** displays an unusual picture: existence of one hexa-coordinated and one penta-coordinated strontium atom side by side in its dimer structure. The introduction of ether groups as coordination sites in complexes **6**-**9** led to decrease in steric hindrance which resulted in the formation of complex **7** as a tetramer. Complex **7** displays a unique Sr_4O_4 cubane core where oxygen atoms undergo μ_3-bridging between strontium atoms. The TG analyses show that the complexes exhibit a step-wise decomposition character, with major mass losses in the region 150−400 °C.

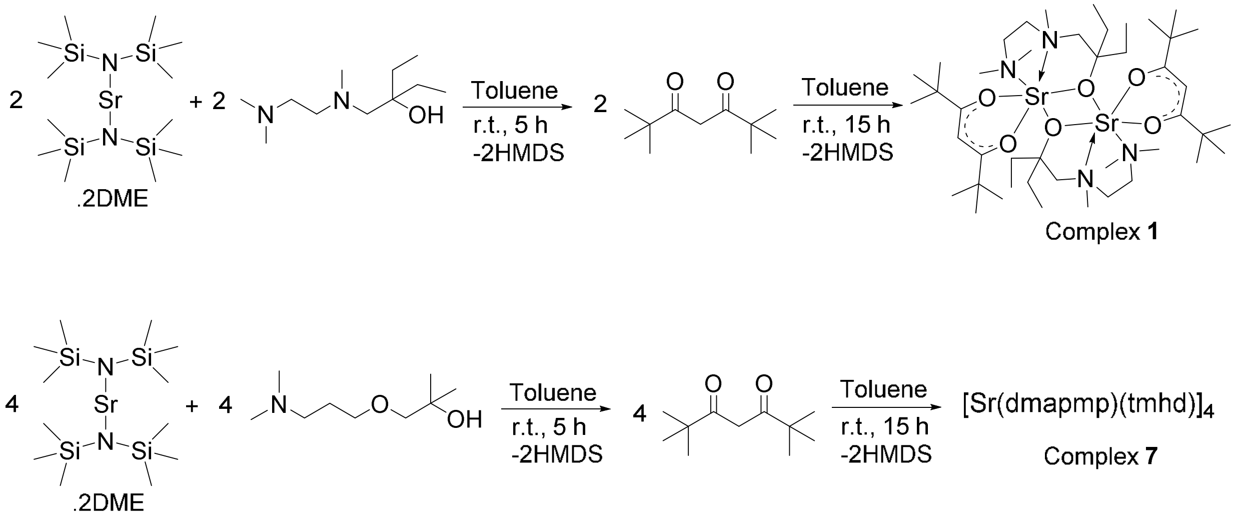
Introduction

The interest in the chemistry of group 2 metals, and especially in strontium is due to their applications in such as insulators for dynamic random access memories,[1] ferroelectrics for computer memory,[2] high-T_c superconductors,[3] electroluminescent films,[4] ionic conductors for fuel cell electrolytes,[5] and mixed-electronic ionic conductors for fuel cell cathodes.[6] All of these applications have required the fabrication of strontium-containing oxide thin films through atomic layer deposition (ALD) or chemical vapor deposition (CVD). For the deposition of thin films using these techniques, strontium precursors with good stability and volatility are essential.

The development of strontium precursors has often been a challenge because of the formation of oligomeric compounds with low solubility and poor volatility as a result of the large size of heavier group 2 ions which makes ligand selection extremely difficult. It is well established that the kinetic stability of many complexes depends on a delicate balance between steric effects, metal size, ligand basicity, and solubility equilibria. Therefore, the ligands introduced should be of large size and possess multiple coordination sites to saturate the metal center as well as forming a strong bond with the metal such that the complex remains stable at high temperatures.

The commonly used strontium precursors are developed using sterically bulky 2,2,6,6-tetramethyl-3,5-heptanedionate (tmhd)[7] or substituted cyclopentadienyl derivatives.[8] The introduction of functionalities to the ligands of a known precursor has been the usual way to achieve a given requirement in the case of homoleptic strontium precursors. However, owing to the uniformity of the ligands, it is difficult for a homoleptic metal precursor to adopt the desired reactivity and stability. The recent development in heteroleptic precursor chemistry[9] of various metals shows the advantage of having two different ligands in a metal complex which gives an interesting alternative with high volatility, good stability, and the desired reactivity. The careful selection of ligands according to needs may lead to a suitable precursor with the desired properties in heteroleptic complexes. The previously reported heteroleptic strontium precursor[10] justified the above by exhibiting enhanced volatility and stability compared to the respective homoleptic complexes.

Our recently reported group 2 metal precursors with 1-((2-(dimethylamino)ethyl)(methyl)amino)-2-methylpropan-2-olate (demamp) and tmhd as coordinating ligands,[10] exhibit good physical properties compared to their respective homoleptic parent compounds, especially in the case of strontium metal. In this paper, we extend our work on heteroleptic strontium



Scheme 1. Synthesis of complex **1** and **7**.

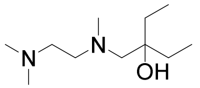
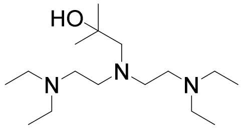
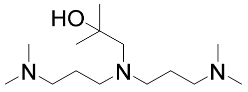
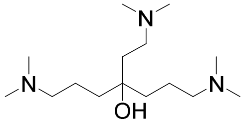
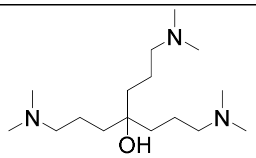
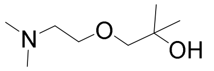
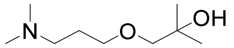
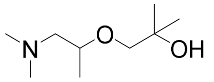
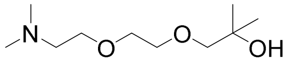
precursors by using 2,2,6,6-tetramethyl-3,5-heptanedione (tmhdH) in combination with various aminoalcohols.

Results and discussion

The recently reported volatile heteroleptic complex Sr(demamp)(tmhd)]$_2$,[10] displays a dimeric structure in which the strontium atoms are held together by oxygen atoms from two demamp group through μ_2-bridging. The volatility of the compounds is inversely related to the molecular weight and thus to the oligomerization. To overcome the dimerization of this type of compound, we employed several aminoalcohol ligands with larger alkyl groups attached to the alkoxy carbon atom and introduced more coordination sites within the ligand to saturate the strontium ion. The aminoalcohols we used (table 1) in combination with tmhdH are, 3-(((2-(dimethylamino)ethyl)(methyl)amino) methyl)pentan-3-ol (dmaemampH) for **1**, 1-(bis(2-(diethylamino)ethyl)amino)-2-methylpropan-2-ol (bdeaeampH) for **2**, 1-(bis(3-(dimethylamino)propyl)amino)-2-methylpropan-2-ol (bdmapampH) for **3**, 1,7-bis(dimethylamino)-4-(2-(dimethylamino)ethyl)heptan-4-ol (bdmadmaehH) for **4**, 1,7-bis(dimethylamino)-4-(3-(dimethylamino)propyl)heptan-4-ol (bdmadmaphH) for **5**, 1-(2-(dimethylamino)ethoxy)-2-methylpropan-2-ol (dmaempH) for **6**, 1-(3-(dimethylamino) propoxy)-2-methylpropan-2-ol (dmapmpH) for **7**, 1-((1-(dimethylamino)propan-2-yl)oxy)-2-methylpropan-2-ol (dmamempH) for **8**, and 1-(2-(2-(dimethylamino)ethoxy) ethoxy)-2-methylpropan-2-ol (dmaeempH) for **9**. Among these, dmaemampH, dmaempH, dmapmpH, and dmamempH are tridentate while bdeaeampH, bdmapampH, bdmadmaehH, bdmadmaphH, and dmaeempH are tetradentate ligands.

The crystal structure analyses of **1**, **2**, **4**, and **5** revealed that all these complexes were crystallized in the monoclinic crystal system and as dimers where the strontium atoms were held together through the oxygen atoms of

Table 1. Aminoalkoxide ligands used in complexes **1**-**9**.

Compound	Ligand used	Ligand structure
1	dmaemampH	
2	bdeaeampH	
3	bdmapampH	
4	bdmadmaehH	
5	bdmadmaphH	
6	dmaempH	
7	dmapmpH	
8	dmamempH	
9	dmaeempH	

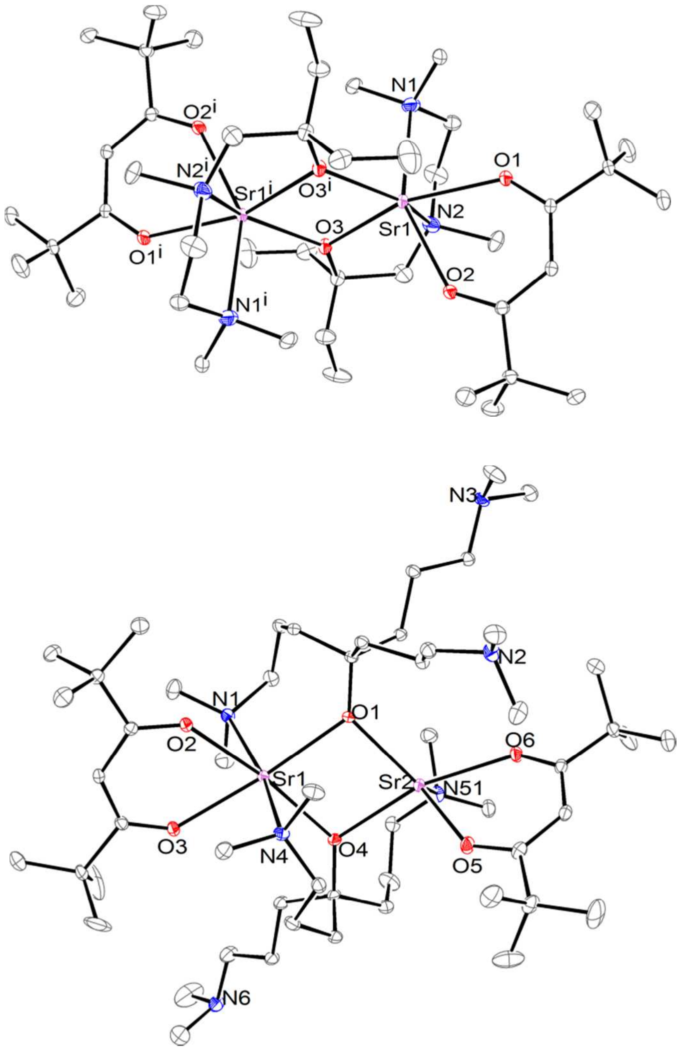


Figure 1. Crystal structure of complex **1** (above) & **2** (below) (disorders were avoided for clarity).

aminoalkoxide ligands by μ_2-bridging. Even though the ligands were bulky and had higher-coordination sites, the formation of dimers revealed the stability possessed by these dimeric structures, which are unaffected by the introduction of a variety of aminoalkoxide ligands. From the available crystal data, it is clear that irrespective of their coordination ability, all the ligands remained tri-coordinated, sometimes even bi-coordinated (in **5**) with strontium metal, and the rest of the coordination sites remained uncoordinated in their complexes. There were several thermal disorders in the crystal structures of these complexes especially in the aminoalkoide part, detailed structures with disorders are given in the supporting information (Figure S1 and Figure S2). But the introduction of less steric ether groups as coordination sites at the expense of amine groups in complexes **6-9** has an effect on complex structures. The complex **7** formed as a tetramer with a Sr_4O_4 cubane core. The alkoxide oxygen atoms in **7** undergoes μ_3-bridging between three strontium atoms whereas the ether oxygen coordinated to individual strontium atoms and the terminal amine group remained uncoordinated. The formation

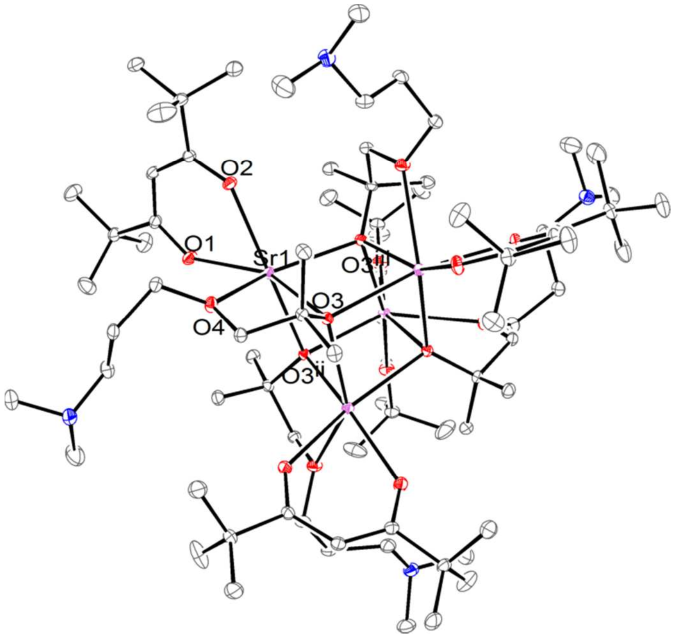


Figure 2. Crystal structure of complex 7.

of high nuclear complex might be due to the less steric effects associated with ether groups compared to the tertiary amine groups which allow more flexibility to the ligands in the formation of the complex.

The complexes were prepared through a procedure slightly modified from that in previously published work.[10] The $Sr[N(SiMe_3)_2]_2\cdot 2DME$ solution in toluene was first treated with the corresponding aminoalcohol in equivalent ratio followed by the addition of tmhdH (as shown in scheme 1 for complex **1**), and the resulting reaction mixture was stirred overnight at room temperature to the afford respective complexes **1-9**. The X-ray quality crystals of complexes **1**, **2**, **4**, **5**, and **7** were grown from a saturated hexane solution of the corresponding complexes at -30 °C.

Complex **1** crystallized in the $P2_1$/n space group (Figure 1), in which one 3-(((2-(dimethylamino)ethyl)(methyl)amino) methyl)pentan-3-olate anion, one 2,2,6,6-tetramethyl-3,5-heptanedionato anion and one strontium atom are observed as an asymmetric unit. In **1**, the metal centers appeared to be in a highly distorted octahedral structure, where the alkoxide oxygen bridged two strontium atoms, exactly as reported previously for [Sr(demamp)(tmhd)]$_2$.[10] The introduction of ethyl group (in dmaemamp) to the alkoxide carbon atom compared to methyl groups (in demamp) had little impact on the bonding nature or overall structure of the complex. Complex **2** (Figure S1), which has two 1-(bis(2-(diethylamino)ethyl)amino)-2-methylpropan-2-olate anions, two 2,2,6,6-tetramethyl-3,5-heptanedionato anions and two strontium atoms in its asymmetric unit, crystallized in the monoclinic space group *Pc*. The introduction of an extra coordination site, using a tetradentate bdeaeamp ligand turned out to be less useful as **2** remains in dimer form, making use of only three coordination sites from the bdeaeamp ligand and

Table 2. Selected bond lengths (Å) and bond angles (˚) of **1**, **2, 4,** and **5**.

$[Sr(dmaemamp)(tmhd)]_2$ (**1**)		$[Sr(bdeaeamp)(tmhd)]_2$ (**2**)		$[Sr(bdmadmaeh)(tmhd)]_2$ (**4**)		$[Sr(bdmadmaph)(tmhd)]_2$ (**5**)	
Bond lengths (Å)							
Sr(1)-O(3)i	2.3902(17)	Sr(1)-O(6)	2.399(2)	Sr(1)-O(3)i	2.390(3)	Sr(1)-O(4)	2.443(2)
Sr(1)-O(3)	2.4454(19)	Sr(1)-O(2)	2.433(3)	Sr(1)-O(1)	2.445(3)	Sr(1)-O(3)	2.451(2)
Sr(1)-O(2)	2.4460(18)	Sr(1)-O(3)	2.453(2)	Sr(1)-O(2)	2.457(3)	Sr(1)-O(1)	2.453(2)
Sr(1)-O(1)	2.452(2)	Sr(1)-O(1)	2.480(3)	Sr(1)-O(3)	2.463(3)	Sr(1)-O(2)	2.479(2)
Sr(1)-N(2)	2.693(3)	Sr(1)-N(2)	2.747(3)	Sr(1)-N(2)i	2.771(4)	Sr(1)-N(1)	2.706(3)
Sr(1)-N(1)	2.754(3)	Sr(1)-N(1)	2.866(3)	Sr(1)-N(1)	2.787(4)	Sr(1)-N(4)	2.712(3)
		Sr(2)-O(3)	2.402(2)			Sr(2)-O(1)	2.389(2)
		Sr(2)-O(4)	2.428(3)			Sr(2)-O(4)	2.411(2)
		Sr(2)-O(6)	2.455(2)			Sr(2)-O(6)	2.418(2)
		Sr(2)-O(5)	2.475(3)			Sr(2)-O(5)	2.421(2)
		Sr(2)-N(5)	2.761(3)			Sr(2)-N(51)	2.704(3)
		Sr(2)-N(4)	2.845(3)				
Sr(1)…Sr(1)i	3.6659(12)	Sr(1)…Sr(2)	3.8128(10)	Sr(1)…Sr(1)i	3.7287(10)	Sr(1)…Sr(2)	3.7412(7)
Bond angles (°)							
O(3)i-Sr(1)-O(3)	81.41(6)	O(6)-Sr(1)-O(2)	102.99(9)	O(3)i-Sr(1)-O(1)	166.60(10)	O(4)-Sr(1)-O(3)	105.32(8)
O(3)i-Sr(1)-O(2)	113.30(6)	O(6)-Sr(1)-O(3)	76.52(8)	O(3)i-Sr(1)-O(2)	103.26(9)	O(4)-Sr(1)-O(1)	77.14(7)
O(3)-Sr(1)-O(2)	98.41(6)	O(2)-Sr(1)-O(3)	113.94(8)	O(1)-Sr(1)-O(2)	70.97(9)	O(3)-Sr(1)-O(1)	173.17(8)
O(3)i-Sr(1)-O(1)	121.33(7)	O(6)-Sr(1)-O(1)	101.27(8)	O(3)i-Sr(1)-O(3)	79.61(9)	O(3)-Sr(1)-O(2)	70.42(7)
O(2)-Sr(1)-O(1)	70.94(6)	O(2)-Sr(1)-O(1)	69.90(8)	O(1)-Sr(1)-O(3)	112.95(9)	O(1)-Sr(1)-O(2)	108.33(7)
O(3)i-Sr(1)-N(2)	141.51(8)	O(3)-Sr(1)-O(1)	175.83(8)	O(2)-Sr(1)-O(3)	99.36(9)	O(4)-Sr(1)-N(1)	105.98(9)
O(3)-Sr(1)-N(2)	66.75(7)	O(6)-Sr(1)-N(2)	114.02(9)	O(3)i-Sr(1)-N(2)i	81.01(12)	O(3)-Sr(1)-N(1)	86.92(8)
O(2)-Sr(1)-N(2)	92.99(7)	O(3)-Sr(1)-N(2)	95.13(9)	O(1)-Sr(1)-N(2)i	86.61(12)	O(1)-Sr(1)-N(1)	86.28(8)
O(1)-Sr(1)-N(2)	92.96(8)	O(1)-Sr(1)-N(2)	82.49(9)	O(2)-Sr(1)-N(2)i	87.78(11)	O(2)-Sr(1)-N(1)	84.47(9)
O(3)i-Sr(1)-N(1)	96.89(7)	O(2)-Sr(1)-N(1)	95.75(9)	O(3)i-Sr(1)-N(1)	101.70(11)	O(4)-Sr(1)-N(4)	85.60(9)
O(3)-Sr(1)-N(1)	96.20(8)	O(3)-Sr(1)-N(1)	66.39(8)	O(1)-Sr(1)-N(1)	84.73(11)	O(3)-Sr(1)-N(4)	87.41(9)
O(1)-Sr(1)-N(1)	84.81(8)	O(1)-Sr(1)-N(1)	115.48(9)	O(3)-Sr(1)-N(1)	84.57(11)	O(1)-Sr(1)-N(4)	99.18(8)
N(2)-Sr(1)-N(1)	67.14(8)	N(2)-Sr(1)-N(1)	67.19(9)	N(2)i-Sr(1)-N(1)	96.67(12)	O(2)-Sr(1)-N(4)	83.79(8)
Sr(1)i-O(3)-Sr(1)	98.59(6)	Sr(2)-O(3)-Sr(1)	103.52(8)	Sr(1)i-O(3)-Sr(1)	100.39(9)	Sr(2)-O(4)-Sr(1)	100.85(8)
		Sr(1)-O(6)-Sr(2)	103.53(8)			Sr(2)-O(1)-Sr(1)	101.18(8)
		O(3)-Sr(2)-O(4)	103.26(9)			O(1)-Sr(2)-O(4)	78.98(7)
		O(3)-Sr(2)-O(6)	76.43(8)			O(1)-Sr(2)-O(6)	115.36(8)
		O(4)-Sr(2)-O(6)	111.59(9)			O(4)-Sr(2)-O(6)	165.32(8)
		O(3)-Sr(2)-O(5)	105.75(9)			O(1)-Sr(2)-O(5)	122.26(9)
		O(4)-Sr(2)-O(5)	69.78(9)			O(4)-Sr(2)-O(5)	98.81(8)
		O(6)-Sr(2)-O(5)	177.22(8)			O(6)-Sr(2)-O(5)	71.35(8)
		O(3)-Sr(2)-N(5)	114.26(9)			O(1)-Sr(2)-N(51)	114.46(9)
		O(6)-Sr(2)-N(5)	94.65(9)			O(4)-Sr(2)-N(51)	89.49(8)
		O(5)-Sr(2)-N(5)	82.89(9)			O(6)-Sr(2)-N(51)	87.18(9)
		O(4)-Sr(2)-N(4)	93.14(9)			O(5)-Sr(2)-N(51)	123.24(10)
		O(6)-Sr(2)-N(4)	66.65(8)				
		O(5)-Sr(2)-N(4)	111.06(9)				
		N(5)-Sr(2)-N(4)	67.60(9)				

leaving one amine side chain as a free site. The use of other tetradentate ligands, that is, bdmadmaeh in **4** and bdmadmaph in **5** had a similar effect: only three coordination sites were used to form the dimer complexes and one of the amine side chain remained as a free site. In **5** the Sr(2) appeared as penta-coordinated leaving two of the amine side chains as free sites. Complex **4** crystallized in the $P2_1/n$ space group (Figure S2), in which one 1,7-bis(dimethylamino)-4-(2-(dimethylamino) ethyl)heptan-4-olate anion, one 2,2,6,6-tetramethyl-3,5-heptanedionato anion, and one strontium atom are observed as an asymmetric unit, whereas in **5** (Figure 1), two strontium atoms, two 1,7-bis(dimethylamino)-4-(3-(dimethylamino) propyl)heptan-4-olate anions, and two 2,2,6,6-tetramethyl-3,5-heptanedionato anions are observed as an asymmetric unit. In complexes **4** and **5**, apart from the bridging of the strontium atoms with alkoxide μ_2-oxygens, the amine side chains play an important role in dimer formation by holding together both the strontium atoms with coordinate bonds (N(1) bonding to Sr(1), N(2) bonding to Sr(1^i), and N(3) remaining free in **4**; and N(4) bonding to Sr(1), N(5) bonding to Sr(2), and N(6) remaining

Table 3. Selected bond lengths (Å) and bond angles (°) of **7**.

(**7**)	
Bond lengths (Å)	
Sr(1)-O(1)	2.432(2)
Sr(1)-O(2)	2.440(2)
Sr(1)-O(3)i	2.509(2)
Sr(1)-O(3)ii	2.546(2)
Sr(1)-O(3)	2.554(2)
Sr(1)-O(4)	2.557(2)
O(3)-Sr(1)ii	2.510(2)
O(3)-Sr(1)i	2.547(2)
Sr(1)…Sr(1)iii	3.8389(8)
Sr(1)…Sr(1)i	3.8979(7)
Sr(1)…Sr(1)ii	3.8980(7)
Bond angles (°)	
O(1)-Sr(1)-O(2)	70.61(8)
O(1)-Sr(1)-O(3)i	123.94(8)
O(2)-Sr(1)-O(3)i	96.92(8)
O(1)-Sr(1)-O(3)ii	98.41(8)
O(2)-Sr(1)-O(3)ii	164.54(8)
O(3)i-Sr(1)-O(3)ii	79.97(8)
O(1)-Sr(1)-O(3)	155.98(8)
O(2)-Sr(1)-O(3)	115.82(8)
O(3)i-Sr(1)-O(3)	79.38(8)
O(3)ii-Sr(1)-O(3)	78.70(8)
O(1)-Sr(1)-O(4)	92.80(8)
O(2)-Sr(1)-O(4)	82.98(8)
O(3)i-Sr(1)-O(4)	141.20(7)
O(3)ii-Sr(1)-O(4)	109.01(8)
O(3)-Sr(1)-O(4)	66.32(7)
Sr(1)ii-O(3)-Sr(1)i	98.80(7)
Sr(1)ii-O(3)-Sr(1)	100.67(8)
Sr(1)i-O(3)-Sr(1)	99.68(8)

free in **5**). Considering the bonding pattern in other strontium complexes of same category, this type of cross bridging is quite unusual. In **5** Sr(2) remained penta-coordinated, going against the common trend in these complexes to acquire a distorted octahedron (like Sr(1) in the same molecule). This is because of the unusual tilting of the tmhd group attached to Sr(2) by about 80.47(11)°, which creates significant hindrance to possible amine coordination with Sr(2) (the two planes that hold the two tmhd groups in these dimer complexes appear in parallel to each other with angles between the planes of 0° in **1**, **4**, and in [Sr(demamp)(tmhd)]$_2$ but 9.62(23)° in **2**). The Sr(2) atom in **5** displays a distorted square-pyramidal structure where the amine occupies the top of the pyramid. The distance between the two metal centers in the dimeric structures were 3.6659(12), 3.8128(10), 3.7287(10), and 3.7412(7) Å for **1**, **2**, **4**, and **5**, respectively (table 2), which are within the range observed for the [Sr(demamp)(tmhd)]$_2$[10] complex (3.7119(6)), but shorter than those of other reported oxygen bridged complexes of strontium, such as the dinuclear complexes [Sr$_2$(tmhd)$_4$(HOCH$_2$CH$_2$OMe)$_2$],[11] and [Sr$_2$(tmhd)$_4$(dmaeH)$_2$ (μ_2-dmaeH)$_2$],[12] where the distance between the metal centres are 4.039(2) and 4.435(2) Å, respectively. The average distances between the strontium metal and the μ_2-bridging alkoxide oxygen atoms are 2.4178(18) Å in **1**, 2.426(2) Å in **2**, 2.4265(3) Å in **4**, and 2.448 (2) Å in **5**, which are in the range seen for [Sr(demamp)(tmhd)]$_2$ (2.416(2) Å), but shorter than the Sr—O bonds (2.728(6) and 2.796(6)) in [Sr$_2$(tmhd)$_4$(dmaeH)$_2$(μ_2-dmaeH)$_2$].[12] The bridging angles (∠M—O—M) observed in these complexes (98.59(6)° in **1**, 103.52(8)° in **2**, 100.39(9)° in **4**, and 100.85(8)° in **5**) are comparable with that observed in [Sr(demamp)(tmhd)]$_2$ (104.58(5)°). Attempts to produce X-ray quality crystals of **3** were unsuccessful even with several attempts. However, with the support of all identified structures of this class of compounds, we expect that the overall structure complex **3** might be similar to those of others.

Complex **7** crystallized in the $I4_1/a$ space group (Figure 2), in which one 1-(3-(dimethylamino) propoxy)-2-methylpropan-2-olate (dmapmp) anion, one 2,2,6,6-tetramethyl-3,5-heptanedionato anion and one strontium atom are observed as an asymmetric unit. The introduction of ether oxygen as a coordination site in **7** compared to the amine nitrogen atoms of complexes **1-5** resulted in formation of tetrameric complex. The μ_3-bridging of alkoxide oxygen atoms between three strontium metal atoms afforded Sr$_4$O$_4$ cubane core for the complex which is observed for the first time in strontium complexes although this type of metal-oxygen cubane structural motif was reported for other metals.[13] The ether oxygen atoms of four dmapmp ligands were coordinated to single strontium atoms each and the terminal amine groups were left uncoordinated. The coordination of two oxygen atoms from the tmhd ligands to each of the strontium atoms completes the coordination sphere where, the strontium atoms in hexacoodinated state with a distorted octahedral structure. The introduction of ether group as coordination sites in complexes **6-9** compared to the amine groups in **1-5** has a dramatic effect in complex formation. The low steric hindrance exerted by the ether group allowed the formation of high nuclear complex for **7** whereas; in **1-5** all complexes remained as dimers. There may a similar effect in other complexes (**6**, **8**, and **9**) where ether group is present as coordination site, but we were unsuccessful in obtaining quality crystals for those complexes to conclude its structure.

The NMR spectra of the complexes were recorded using C$_6$D$_6$ as solvent and standard at room temperature. The ^{1}H NMR spectra of all the complexes exhibit broadness in the aminoalkoxide protons, especially for those that are closer to the coordinating nitrogen atoms (detailed assignments of identified individual protons are given in the experimental section). The chemical shifts observed for the ligand protons in the complexes, and the absence of any –OH peak, confirmed the successful coordination of the corresponding aminoalkoxide and tmhd ligands to the strontium metal. The tmhd protons display comparatively sharper peaks. The two tmhd tertiary butyl groups from complexes **1-9** resonate as singlets at δ = 1.33, 1.38, 1.34, 1.34, 1.33, 1.33, 1.35, 1.33, and 1.35 ppm respectively, while the β-CH resonate at δ = 5.84, 5.87, 5.88, 5.84, 5.84, 5.85, 5.90, 5.86, and 5.85 ppm according to the order. Broad NMR peaks were reported in this work and other aminoalkoxide strontium complexes[10,14] may be due to the slow site exchange in solution at NMR time scale. To examine possible structural changes in solution compound **1** was studied through VT-NMR experiments in which tmhd peaks remained as singlets and did not provid any proof for dissociation of the complex **1** in solution.

In literature the tmhd complexes and alkoxide complexes of strontium displayed structural changes and solvent coordination with the polar solvents used.[15] So we repeated the synthesis of complex **1** and **7** in polar solvents like THF, diethyl ether, and DME to examine the stability of these complexes in different solvents. To our surprise none of the polar solvents coordinated to metal and the complexes **1** and **7** were obtained in pure form from those polar solvents. The products were isolated and characterized by NMR, IR and elemental analysis to confirm the results. This result shows stability of $[Sr(aminoalkoxide)(tmhd)]_x$ complexes which are unaffected by the presence coordinating polar solvents.

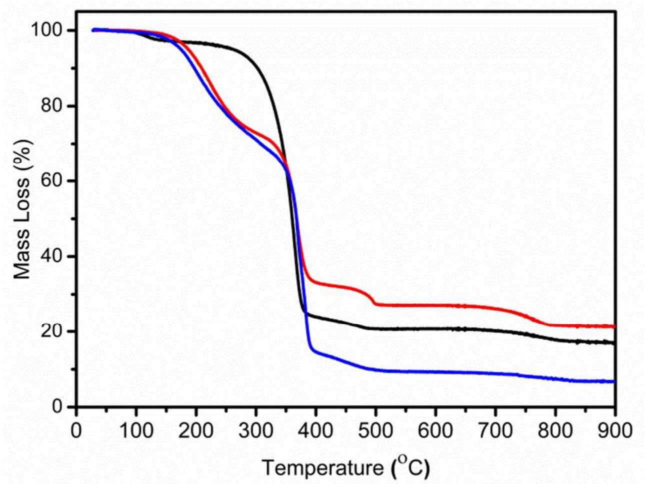


Figure 3. TGA plots of $[Sr(dmaemamp)(tmhd)]_2$ (**1**) (black), $[Sr(bdeaeamp)(tmhd)]_2$ (**2**) (red), and $[Sr(bdmapamp)(tmhd)]_2$ (**3**) (blue).

Thermo-gravimetric analyses of products **1-9** were conducted from room temperature to 900 °C (Figures 3, S4, S5). Prior to the analyses, sampling was carried out in an argon filled glove box, and data collection was performed under a constant flow of nitrogen to avoid any air contact. The TGA plot of compound **1** displays 5% loss in mass from 100 to 250 °C, followed by 71% loss up to 400 °C and further 4% up to 500 °C. The first step may be due to the evaporation of any trapped solvent in the complex, whereas, the major weight loss at 250–400 °C might be due to the evaporation of a part of the compound and possible decomposition of the product and the third mass loss should be attributed to the evaporation of a portion of the decomposition products. Compounds **2-5** show a step like character in their TG curves, with mass losses of 26% (150−300 °C), 40% (300–400 °C), and 6% (400–500 °C) for **2**, 31% (120−325 °C), 54% (325–400 °C), and 4.4% (400–500°C) for **3**, 33% (150–275 °C), 42% (275−380 °C), and 5% (380–500 °C) for **4**, 40% (150–330 °C), 36% (330–400 °C), and 3% (400–500 °C) for **5**. Compounds **6-9** exhibit a similar pattern in their respective TGA plots, in which a considerable loss of mass can be seen from room temperature to 300 °C, that is, 4%, 6%, 16%, and 11%, respectively, followed by a major mass loss of 56%, 60%, 61%, and 59%, respectively in the region of 300–400 °C. Further mass losses were observed in these complexes up to 500 °C as 7%, 4%, 3%, and 5%, respectively. The stepwise decomposition pattern displayed by the complexes in the TG analyses and relatively high amount of residues (except for **3**) indicate the self-decomposition of the complexes during the TG analysis, which reflects the temperature instability of the complexes. As all possibilities of contact with air and oxygen were avoided, the residue is thought to be a mixture of strontium oxide and non-volatile fractions as a result of ligand decomposition. The calculation based on the molecular weights of the compounds agrees with the above assumption. The study of the volatile character for the compounds at reduced pressure (0.5Torr) resulted in decomposition of complexes **6-9** at 150 °C whereas, complexes **1-5** display stable character throughout the experiment.

Experimental

General Remarks

NMR spectra were recorded on a Bruker 300 MHz spectrometer with C_6D_6 as solvent and standard. IR spectra were obtained with a Nicolet Nexus FT-IR spectrophotometer. Elemental analyses were carried out on a ThermoScientific OEA Flash 2000 Analyzer. Thermo-gravimetric analyses were conducted on a SETARAM 92-18 TG-DTA instrument with a constant flow of nitrogen throughout the experiment. $Sr[N(SiMe_2)_2]_2 \cdot 2DME$,[16] and the aminoalcohols, bdeaeampH,[14b] bdmapampH,[14b] dmapmpH,[17] dmaeempH,[17] dmaempH,[17] dmamempH,[17] and 2,2-diethyloxirane[18] were prepared according to the literature methods. All reactions were carried out in inert dry conditions using standard Schlenk techniques or in an argon filled-glove box. Hexane and toluene were purified with an Innovative Technology PS-MD-4 solvent purification system. All other chemicals were purchased from Aldrich and used as received.

Syntheses

3-(((2-(dimethylamino)ethyl)(methyl)amino)methyl)pentan-3-ol (dmaemampH): 2,2-Diethyloxirane (10.0 g, 0.10 mol) was added drop wise at 0 °C with constant stirring to a 40% water solution of trimethylethane-1,2-diamine (10.2 g, 0.10 mol) taken in a three-necked flask fitted with a reflux condenser. After the addition, the reaction mixture was allowed to warm up to room temperature and stirring was continued for another six hours. Then, the product was extracted three times with ether (50 mL×3) and the combined organic layer was washed with brine. The solvent was removed, and the residue was distilled (60 °C/0.5 Torr) to obtain the pure product as a colorless liquid. Yield 14.2 g (70%). FTIR (ν_{max}/cm^{-1}) 3375 (OH). Found: C, 65.28; H, 12.92; N, 13.86. Calc. for $C_9H_{22}N_2O$: C, 65.30; H, 12.95%; N, 13.84. δ_H (300 MHz; C_6D_6; TMS) 0.97 (6 H, t, $OC(CH_2C\mathit{H}_3)_2$), 1.57 (4 H, m, $OC(C\mathit{H}_2CH_3)_2$), 2.02 (6 H, s, $N(C\mathit{H}_3)_2$), 2.10 (2 H, t, $(CH_3)_2NC\mathit{H}_2$), 2.21 (3 H, s, $N(C\mathit{H}_3)$), 2.24 (2 H, s,

$N(CH_3)CH_2$), 2.32 (2 H, t, $(CH_3)_2NCH_2CH_2$), 5.25 (1 H, s, O*H*).

1,7-bis(dimethylamino)-4-(2-(dimethylamino)ethyl)heptan-4-ol (bdmadmaehH) : Methyl 3-(dimethylamino)propanoate (5.07 g, 0.040 mol) in 200 mL anhydrous benzene was added drop wise under nitrogen to a stirred solution of 3-dimethylaminopropylmagnesium chloride prepared from dry magnesium turnings (2.94 g, 0.12 mol) and 3-dimethylaminopropyl chloride (14.1 g, 0.11 mol) in anhydrous THF (100 mL). The reaction mixture was heated at reflux for 10 h and then cooled in an ice bath and hydrolyzed by adding a saturated solution of ammonium chloride (50 mL). The organic layer was separated and the aqueous solution extracted with diisopropyl ether (10 × 50 mL). The organic solutions were combined and dried over Na_2SO_4. The solvent was evaporated to give the crude product. The purified product was collected by distillation (125 °C/0.02 Torr) as a colorless liquid. Yield 5.00 g (47%). FTIR (ν_{max}/cm^{-1}) 3254 (OH). Found: C, 65.83; H, 12.90; N, 15.39. Calc. for $C_9H_{22}N_2O$: C, 65.88; H, 12.90; N, 15.37%. δH (300 MHz; C_6D_6; TMS) 1.52-1.65 (10 H, m, $(CH_2CH_2CH_2)_2C(OH)CH_2CH_2$), 1.98 (6 H, s, $CH_2CH_2N(CH_3)_2$), 2.11 (12 H, s, 2 $(CH_2CH_2CH_2N(CH_3)_2)$, 2.22 (4 H, t, 2 $(CH_2CH_2CH_2N(CH_3)_2)$, 2.33 (2 H, t, $CH_2CH_2N(CH_3)_2$), 5.87 (1 H, s, O*H*).

1,7-bis(dimethylamino)-4-(3-(dimethylamino)propyl) heptan-4-ol (bdmadmaphH): A similar procedure was followed to that described above, but using methyl 4-(dimethylamino) butanoate (5.80 g, 0.040 mol). The purified product was collected by distillation (130 °C/0.02 Torr) as a colorless liquid. Yield 2.80 g (25%). FTIR (ν_{max}/cm^{-1}) 3196 (OH). Found: C, 66.53; H, 12.95; N, 14.65. Calc. for $C_9H_{22}N_2O$: C, 66.85; H, 12.97%; N, 14.62. δH (300 MHz; C_6D_6; TMS) 1.53-1.65 (12 H, m, $(CH_2CH_2CH_2)_3C(OH)$), 2.08 (18 H, s, 3 $(N(CH_3)_2)$, 2.18 (6 H, t, $(CH_2CH_2CH_2)_3C(OH)$), 5.79 (1 H, s, O*H*).

General Procedure for $[Sr(Aminoalkoxide)(tmhd)]_2$ Complexes:

The aminoalcohol in toluene (5 mL) was added dropwise at room temperatures to a solution of $Sr(btsa)_2{\cdot}2DME$ in toluene (15 mL) under stirring., After stirring for 5 h at room temperature, 2,2,6,6-tetramethyl-3,5-heptanedione (tmhdH) was added to the reaction mixture, which was then stirred for another 15 h at room temperature. Then, the solvent was evaporated and the residue was extracted with hexane, filtered, and dried to obtain the product. X-ray quality crystals were grown from concentrated hexane solutions upon cooling.

$[Sr(dmaemamp)(tmhd)]_2$ (1): $Sr(btsa)_2{\cdot}2DME$ (0.590 g, 1.0 mmol), 3-(((2-(dimethylamino)ethyl)(methyl)amino)methyl) pentan-3-ol (dmaemampH) (0.202 g, 1.0 mmol), and 2,2,6,6-tetramethyl-3,5-heptanedione (tmhdH) (0.184 g, 1.0 mmol) were used. Yield 0.420 g (89%). FTIR (ν_{max}/cm^{-1}) 2961s, 2864w, 1590vs, 1576m, 1534w, 1504m, 1456m, 1420vs, 1354w, 1224w, 1186w, 1126w, 1038w, 863w, 789(w), 751w, 470w. Found: C, 54.76; H, 9.12; N, 5.70. Calc. for $C_{44}H_{88}N_4O_6Sr_2$: C, 55.96; H, 9.39; N, 5.93%. δH (300 MHz; C_6D_6; TMS) 0.91 (6 H, br m, $OC(CH_2CH_3)_2$), 1.33 (18 H, s, $C(CH_3)_3$), 1.2-1.8 (4 H, br m, $OC(CH_2CH_3)_2$), 2.0-2.4 (11 H, br m), 2.50 (4 H, br s), 5.84 (1 H, s, β-C*H*). EI-MS: *m/z* calc. for $[Sr(dmaemamp)(tmhd)]_2$: 944.48 $[M]^+$; Found 725 $[Sr_2(tmhd)_3]^+$, 271 $[Sr(tmhd)]^+$.

$[Sr(bdeaeamp)(tmhd)]_2$ (2): $Sr(btsa)_2{\cdot}2DME$ (0.590 g, 1.0 mmol), 1-(bis(2-(diethylamino)ethyl)amino)-2-methylpropan-2-ol (bdeaeampH) (0.288 g, 1.0 mmol) and 2,2,6,6-tetramethyl-3,5-heptanedione (tmhdH) (0.184 g, 1.0 mmol) were used. Yield 0.510 g (92%). FTIR (ν_{max}/cm^{-1}) 2967s, 2814w, 1591s, 1576m, 1534w, 1503m, 1455m, 1417vs, 1387m, 1356m, 1220w, 1181w, 1129w, 1058w, 976w, 863w, 789w, 731w, 468w. Found: C, 58.07; H, 9.89; N, 7.40. Calc. for $C_{54}H_{110}N_4O_6Sr_2$: C, 58.18; H, 9.95; N, 7.54%. δH (300 MHz; C_6D_6; TMS) 1.04 (12 H, t, $N(CH_2CH_3)_2$), 1.38 (18 H, s, $C(CH_3)_3$), 1.44 (6 H, s, $C(CH_3)_2O$), 2.30-2.90 (18 H, br), 5.87 (1 H, s, β-C*H*). EI-MS: m/z calc. for $[Sr(bdeaeamp)(tmhd)]_2$: 1086.65 $[M]^+$; Found 725 $[Sr_2(tmhd)_3]^+$, 271 $[Sr(tmhd)]^+$.

$[Sr(bdmapamp)(tmhd)]_x$ (3): $Sr(btsa)_2{\cdot}2DME$ (0.590 g, 1.0 mmol), 1-(bis(3-(dimethylamino)propyl)amino)-2-methylpropan-2-ol (bdmapampH) (0.260 g, 1.0 mmol) and 2,2,6,6-tetramethyl-3,5-heptanedione (tmhdH) (0.184 g, 1.0 mmol) were used. Yield 0.490 g (93%). FTIR (ν_{max}/cm^{-1}) 2950s, 2862w, 2814w, 2783w, 1592s, 1577m, 1534w, 1504m, 1457m, 1417vs, 1388m, 1358m, 1224w, 1183w, 1128w, 1041w, 864w, 791w, 755w, 473w. Found: C, 56.40; H, 9.62; N, 8.06. Calc. for $C_{50}H_{102}N_4O_6Sr_2$: C, 56.73; H, 9.71; N, 7.94%. δH (300 MHz; C_6D_6; TMS) 1.34 (18 H, br s, $C(CH_3)_3$), 1.61 (10 H, br s, $C(CH_3)_2$ and $CH_2CH_2CH_2$), 2.11(16 H, s+m, $N(CH_3)_2$ and $CH_2CH_2CH_2$), 2.23 (4 H, t, $CH_2CH_2CH_2$), 2.61 (2 H, br s, $CH_2C(CH_3)_2$), 5.88 (1 H, s, β-C*H*). EI-MS: *m/z* calc. for $[Sr(bdmapamp)(tmhd)]_2$: 1030.59 $[M]^+$; Found 725 $[Sr_2(tmhd)_3]^+$, 271 $[Sr(tmhd)]^+$.

$[Sr(bdmadmaeh)(tmhd)]_2$ (4): $Sr(btsa)_2{\cdot}2DME$ (0.590 g, 1.0 mmol), 1,7-bis(dimethylamino)-4-(2-(dimethylamino)ethyl) heptan-4-ol (bdmadmaehH) (0.274 g, 1.0 mmol) and 2,2,6,6-tetramethyl-3,5-heptanedione (tmhdH) (0.184 g, 1.0 mmol) were used. Yield 0.480 g (88%). FTIR (ν_{max}/cm^{-1}) 2949s, 2862w, 2813w, 2782w, 1590s, 1576m, 1533w, 1504m, 1452m, 1415vs, 1387m, 1356m, 1223w, 1183w, 1128w, 1041w, 864w, 789w, 752w, 471w. Found: C, 57.31; H, 9.81; N, 7.68. Calc. for $C_{52}H_{106}N_6O_6Sr_2$: C, 57.47; H, 9.83; N, 7.73%. δH (300 MHz; C_6D_6; TMS) 1.34 (18 H, s, $C(CH_3)_3$), 1.50 (10 H, br m, $(CH_2CH_2CH_2)_2C(OH)CH_2CH_2$), 2.06 (6 H, s, $CH_2CH_2N(CH_3)_2$), 2.27 (16 H, br s, $CH_2CH_2CH_2N(CH_3)_2$ and $CH_2CH_2N(CH_3)_2$), 2.75 (2 H, br s, $CH_2CH_2CH_2N(CH_3)_2$), 5.84 (1 H, s, β-C*H*). EI-MS: *m/z* calc. for $[Sr(bdmadmaeh)(tmhd)]_2$: 1086.63 $[M]^+$; Found 725 $[Sr_2(tmhd)_3]^+$, 271 $[Sr(tmhd)]^+$.

$[Sr(bdmadmaph)(tmhd)]_2$ (5): $Sr(btsa)_2{\cdot}2DME$ (0.590 g, 1.0 mmol), 1,7-bis(dimethylamino)-4-(3-(dimethylamino)propyl) heptan-4-ol (bdmadmaphH) (0.288 g, 1.0 mmol) and 2,2,6,6-tetramethyl-3,5-heptanedione (tmhdH) (0.184 g, 1.0 mmol) were used. Yield 0.500 g (90%). FTIR (ν_{max}/cm^{-1}) 2947s, 2863w, 2814w, 2778w, 1591s, 1577m, 1534w, 1503m, 1451m, 1417vs, 1388m, 1358m, 1272w, 1183w, 1128w, 1040w, 864w, 790w, 755w, 472w. Found: C, 57.95; H, 9.94; N, 7.45. Calc. for $C_{54}H_{110}N_6O_6Sr_2$: C, 58.18; H, 9.95; N, 7.54%. δH (300 MHz;

$\mathrm{C_6D_6}$; TMS) 1.33 (18 H, s, $\mathrm{C(C}H_3)_3$), 1.54 (6 H, br m, $\mathrm{C}H_2\mathrm{CH_2CH_2N(CH_3)_2}$), 1.67 (6 H, br m, $\mathrm{CH_2C}H_2\mathrm{CH_2N(CH_3)_2}$), 2.18 (18 H, s, $(\mathrm{C}H_3)_2\mathrm{N}$), 2.40 (6 H, br m, $\mathrm{CH_2CH_2C}H_2\mathrm{N(CH_3)_2}$), 5.84 (1 H, s, β-C*H*). EI-MS: *m*/*z* calc. for [Sr(bdmadmaph)(tmhd)]$_2$: 1114.66 [*M*]$^+$; Found 725 $[\mathrm{Sr_2(tmhd)_3}]^+$, 271 $[\mathrm{Sr(tmhd)}]^+$.

[Sr(dmaemp)(tmhd)]$_x$ (6): Sr(btsa)$_2$·2DME (0.590 g, 1.0 mmol), 1-(2-(dimethylamino)ethoxy)-2-methylpropan-2-ol (dmaempH) (0.161 g, 1.0 mmol) and 2,2,6,6-tetramethyl-3,5-heptanedione (tmhdH) (0.184 g, 1.0 mmol) were used. Yield 0.370 g (86%). FTIR (ν_{max}/cm^{-1}) 2952s, 2899m, 2866m, 2821w, 2781w, 1596s, 1576m, 1534w, 1503m, 1456s, 1419vs, 1388m, 1358m, 1271w, 1225m, 1184m, 1109m, 1043w, 982w, 945w, 863w, 790w, 752w, 472w. Found: C, 52.41; H, 8.71; N, 3.18. Calc. for $\mathrm{C_{38}H_{74}N_2O_8Sr_2}$: C, 52.93; H, 8.65; N, 3.25%. δH (300 MHz; $\mathrm{C_6D_6}$; TMS) 1.33 (18 H, s, $\mathrm{C(C}H_3)_3$), 1.53 (6 H, br s, $\mathrm{C(C}H_3)_2$), 2.08 (8 H, br s, $(\mathrm{C}H_3)_2\mathrm{N}$ and $\mathrm{OCH_2C}H_2$), 3.24 (2 H, br s, $\mathrm{C(CH_3)_2OC}H_2\mathrm{O}$), 3.46 (2 H, br s, $\mathrm{CH_2OC}H_2$), 5.85 (1 H, s, β-C*H*). EI-MS: *m*/*z* calc. for [Sr(dmaemp)(tmhd)]$_2$: 862.36 [*M*]$^+$; Found 725 $[\mathrm{Sr_2(tmhd)_3}]^+$, 271 $[\mathrm{Sr(tmhd)}]^+$.

[Sr(dmapmp)(tmhd)]$_4$ (7): Sr(btsa)$_2$·2DME (0.590 g, 1.0 mmol), 1-(3-(dimethylamino)propoxy)-2-methylpropan-2-ol (dmapmpH) (0.175 g, 1.0 mmol) and 2,2,6,6-tetramethyl-3,5-heptanedione (tmhdH) (0.184 g, 1.0 mmol) were used. Yield 0.390 g (88%). FTIR (ν_{max}/cm^{-1}) 2952s, 2865w, 2815w, 2765w, 1588s, 1577s, 1535w, 1504m, 1455m, 1413vs, 1388m, 1357m, 1271w, 1183w, 1130w, 1077m, 940w, 864w, 791w, 755w, 471w. Found: C, 53.34; H, 8.92; N, 3.29. Calc. for $\mathrm{C_{40}H_{78}N_2O_8Sr_2}$: C, 53.96; H, 8.83; N, 3.15%. δH (300 MHz; $\mathrm{C_6D_6}$; TMS) 1.35 (18 H, s, $\mathrm{C(C}H_3)_3$), 1.65 (6 H, s, $\mathrm{C(C}H_3)_2$), 1.77 (2 H, m, $\mathrm{(CH_3)_2NCH_2C}H_2\mathrm{CH_2}$), 2.09 (6 H, s, $(\mathrm{C}H_3)_2\mathrm{N}$), 2.21 (2 H, t, $\mathrm{(CH_3)_2NC}H_2\mathrm{CH_2CH_2}$), 3.70 (4 H, m, $\mathrm{(CH_3)_2NCH_2CH_2C}H_2$ and $\mathrm{C(CH_3)_2OC}H_2$), 5.90 (1 H, s, β-C*H*). EI-MS: *m*/*z* calc. for [Sr(dmapmp)(tmhd)]$_2$: 890.39 [*M*]$^+$; Found 725 $[\mathrm{Sr_2(tmhd)_3}]^+$, 271 $[\mathrm{Sr(tmhd)}]^+$.

[Sr(dmamemp)(tmhd)]$_x$ (8): Sr(btsa)$_2$·2DME (0.590 g, 1.0 mmol), 1-((1-(dimethylamino)propan-2-yl)oxy)-2-methylpropan-2-ol (dmamempH) (0.175 g, 1.0 mmol) and 2,2,6,6-tetramethyl-3,5-heptanedione (tmhdH) (0.184 g, 1.0 mmol) were used. Yield 0.380 g (85%). FTIR (ν_{max}/cm^{-1}) 2952vs, 2865s, 2829w, 2781w, 1595vs, 1577s, 1534w, 1504m, 1456s, 1418vs, 1388m, 1359m, 1272w, 1224w, 1184w, 1128w, 1082w, 1051w, 989w, 950w, 863w, 790w, 755w, 472w. Found: C, 52.56; H, 9.02; N, 3.01. Calc. for $\mathrm{C_{40}H_{78}N_2O_8Sr_2}$: C, 53.96; H, 8.83; N, 3.15%. δH (300 MHz; $\mathrm{C_6D_6}$; TMS) 1.23 (3 H, br s, $\mathrm{CH(C}H_3)$), 1.33 (18 H, s, $\mathrm{C(C}H_3)_3$), 1.54 (6 H, br s, $\mathrm{C(C}H_3)_2$), 2.12 (6 H, br s, $(\mathrm{C}H_3)_2\mathrm{N}$), 2.66 (1 H, br s, $\mathrm{N(CH_3)_2C}H_2$), 3.34 (1 H, br s, $\mathrm{C}H\mathrm{(CH_3)OCH_2}$), 3.55 (2H, br s, $\mathrm{CH(CH_3)OC}H_2$), 5.86 (1H, s, β-C*H*). EI-MS: *m*/*z* calc. for [Sr(dmamemp)(tmhd)]$_2$: 890.39 [*M*]$^+$; Found 725 $[\mathrm{Sr_2(tmhd)_3}]^+$, 271 $[\mathrm{Sr(tmhd)}]^+$.

[Sr(dmaeemp)(tmhd)]$_x$ (9): Sr(btsa)$_2$·2DME (0.590 g, 1.0 mmol), 1-(2-(2-(dimethylamino)ethoxy)ethoxy)-2-methyl propan-2-ol (dmaeempH) (0.205 g, 1.0 mmol) and 2,2,6,6-tetramethyl-3,5-heptanedione (tmhdH) (0.184 g, 1.0 mmol) were used. Yield 0.410 g (86%). FTIR (ν_{max}/cm^{-1}) 2950s, 2820w, 2771w, 1593s, 1576m, 1533w, 1504m, 1455s, 1420vs, 1387m, 1357m, 1270w, 1224w, 1184w, 1126m, 1090w, 1052w, 950w, 863w, 789w, 472w. Found: C, 52.34; H, 9.01; N, 2.92. Calc. for $\mathrm{C_{42}H_{82}N_2O_{10}Sr_2}$: C, 53.08; H, 8.70; N, 2.95%. δH (300 MHz; $\mathrm{C_6D_6}$; TMS) 1.35 (18 H, s, $\mathrm{C(C}H_3)_3$), 1.56 (6 H, br s, $\mathrm{C(C}H_3)_2$), 2.12 (6 H, br s, $(\mathrm{C}H_3)_2\mathrm{N}$), 2.37 (2 H, br m, $\mathrm{(CH_3)_2NC}H_2$), 3.52 (8 H, br m), 5.85 (1 H, s, β-C*H*). EI-MS: *m*/*z* calc. for [Sr(dmaeemp)(tmhd)]$_2$: 950.41 [*M*]$^+$; Found 725 $[\mathrm{Sr_2(tmhd)_3}]^+$, 271 $[\mathrm{Sr(tmhd)}]^+$.

Crystallographic Data Collection and Refinement of the Structure

Crystals of complexes **1**, **2**, **4**, **5**, and **7** were coated with paratone oil and the diffraction data were measured at 173 K with Mo K$_\alpha$ radiation on an X-ray diffraction camera system using an imaging plate equipped with a graphite crystal incident beam monochromator. The RapidAuto software[19] was used for data collection and processing. The crystal structures were solved by the direct method with SIR-97 of the WINGX software package[20] and refined by full-matrix least-squares calculations with the SHELXTL software package.[21]

One 3-(((2-(dimethylamino)ethyl)(methyl)amino)methyl) pentan-3-olate anion, one 2,2,6,6-tetramethyl-3,5-heptanedionato anion and one strontium atom were observed as an asymmetric unit for **1**, two 1-(bis(2-(diethylamino)ethyl)amino)-2-methylpropan-2-olate anions, two 2,2,6,6-tetramethyl-3,5-heptanedionato anions and two strontium atoms were observed as an asymmetric unit in **2**, one 1,7-bis(dimethylamino)-4-(2-(dimethylamino)ethyl)heptan-4-olate anion, one 2,2,6,6-tetramethyl-3,5-heptanedionato anion and one strontium atom were observed as an asymmetric unit in **4**, two strontium atoms, two 1,7-bis(dimethylamino)-4-(3-(dimethylamino)propyl)heptan-4-olate anion, and two 2,2,6,6-tetramethyl-3,5-heptanedionato anion were observed as an asymmetric unit in **5**, and one 1-(3-(dimethylamino) propoxy)-2-methylpropan-2-olate (dmapmp) anion, one 2,2,6,6-tetramethyl-3,5-heptanedionato anion and one strontium atom are observed as an asymmetric unit in **7**. All non-hydrogen atoms are refined anisotropically; the hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U (C) and 1.5U (C$_{\mathrm{methyl}}$), and their coordinates were allowed to ride on their respective atoms. In **1**, the least-squares refinement of the structural model was performed under geometry restraint DFIX for the disordered part of a 3-(((2-(dimethylamino)ethyl)(methyl)amino)methyl)-pentan-3-olate anion. Refinement of the structure converged at a final $R1$ = 0.0422 and $wR2$ = 0.0820 for 4152 reflections with $I > 2\sigma(I)$; $R1$ = 0.0770 and $wR2$ = 0.0905 for all 5953 reflections. The largest difference peak and hole were 0.346 and −0.520 e·Å^{-3}, respectively. In **2** the least-squares refinement of the structural model was performed under geometry restraint DFIX and displacement parameter restraint ISOR for disordered part of a 1-(bis(2-(diethylamino)ethyl)amino)-2-methylpropan-2-olate anion. Refinement of the structure converged at a final $R1$ = 0.0383 and $wR2$ = 0.0809 for 10590 reflections with $I > 2\sigma(I)$; $R1$ = 0.0573 and $wR2$ = 0.0919 for all 13398 reflections. The largest difference peak and hole were 0.536 and −0.586 e·Å^{-3}, respectively. In **4**, structural refinement converged to a final value of R1 = 0.0434, $wR2$ = 0.0933 for all 4609 reflections with $I > 2\sigma(I)$; $R1$ = 0.0882, $wR2$ = 0.1429 for all 6938 reflections. The largest difference peak and hole were 0.966 and −1.219 e·Å^{-3}, respectively. In **5**, refinement of the structure converged at a final $R1$ = 0.0540, $wR2$ = 0.0984 for 9012 reflections with $I > 2\sigma(I)$; $R1$ = 0.1068, $wR2$ = 0.1165 for all 14403 reflections. The largest difference peak and hole were 0.725 and –0.499 e·Å^{-3}, respectively. In **7**, refinement of the structure converged at a final $R1$ = 0.0508, $wR2$ = 0.1035 for 3608 reflections with $I > 2\sigma(I)$; $R1$ = 0.0904, $wR2$ = 0.1205 for all 5378 reflections. The largest difference peak and hole were 0.622 and –0.772 e·Å^{-3}, respectively.

CCDC-973486 (**1**), 973487 (**2**), 973488 (**4**), 973489 (**5**), and 1004596 (**7**) contains the supplementary crystallographic data for this paper.

Conclusions

Attempts to synthesize several heteroleptic complexes of strontium with different aminoalkoxide and tmhd ligands were successful. Although the introduction of various aminoalkoxide ligands with increased coordination ability and bulkiness were not successful in making monomeric structures, various structurally interesting strontium complexes were prepared. The strontium atoms in complexes **1-5** used only five or six coordination sites from the several available to form stable dimer structures. The tendency of strontium atoms to form strong μ_2-oxygen bridging with alkoxy group appeared as the setback in our attempts to produce efficient monomer complexes. The crystal structures of **4** and **5** show an interesting bonding nature of amine side chains in which one unit of bdmadmaeh and bdmadmaph form coordination bonds to both the strontium atoms in their respective dimers. Whereas in complexes **6-9** the introduction of ether groups in place of amine groups as coordination sites resulted in formation higher nuclear compounds due to the less steric hindrance in those ligands. Complex **7** formed as tetramer and the alkoxide oxygen undergone μ_3-bridging in the complex which resulted in unique Sr_4O_4 cubane core for the complex. The TG analyses of the complexes display a major weight loss in the region of 250−300 °C for **1** and two-step losses at 150−400 °C for complexes **2-5**, whereas in complexes **6-9** a major loss occurred at 300−400 °C. Studies are in progress on the application of these heteroleptic strontium complexes as possible precursors for the growth of thin films of $SrTiO_3$ (STO) and $Ba_{0.5}Sr_{0.5}TiO_3$ (BSTO). The high solubility of these complexes makes the synthesis of STO nanoparticles in solution phase feasible.

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Notes and references

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† Electronic Supplementary Information (ESI) available: TGA plot of complexes **4-9**. A summary of the crystal and some crystallography data is given in Table S1. ORTEP diagrams of compounds **1**, **2**, and **4** were given with the observed disorders in their crystal structures. ORTEP diagram of the cubane core in **7** was given. See DOI: 10.1039/b000000x/

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Graphical Abstract

Synthesis of heteroleptic strontium complexes containing aminoalkoxide and β-diketonate ligands were demonstrated.