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Salen-Type Compounds of Calcium and Strontium

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Salen complexes of the heavy alkaline-earth metals, calcium and strontium, were prepared by the reaction of various salen(*t*-Bu)H_2 ligands with the metals in ethanol. Six new calcium and strontium compounds, [Ca(salen(*t*-Bu))(HOEt)$_2$(thf)] (**1**), [Ca(salen(*t*-Bu))(HOEt)$_2$] (**2**), [Ca(salpen(*t*-Bu))(HOEt)$_3$] (**3**), [Ca(salophen(*t*-Bu))(HOEt)(thf)] (**4**), [Sr(salen(*t*-Bu))(HOEt)$_3$] (**5**), and [Sr(salophen(*t*-Bu))(HOEt)(thf)$_2$] (**6**), were formed in this way with the quatridentate Schiff-base ligands *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)ethylenediamine (salen(*t*-Bu)H_2), *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,3-propanediamine (salpen(*t*-Bu)H_2), and *N*,*N*′-*o*-phenylenebis(3,5-di-*tert*-butylsalicylideneimine (salophen(*t*-Bu)H_2). Initially, ammonia solutions of the metals were combined with the salen(*t*-Bu)H_2 ligands, and in the reaction of strontium with salen(*t*-Bu)H_2, the unusual tetrametallic cluster [{OC_6H_2(*t*-Bu)$_2$CHN(CH_2)$_2$$NH_2$}Sr($\mu_3$-salean(*t*-Bu)$H_2$)Sr($\mu_3$-OH)]$_2$ (**7**) was produced (salean(*t*-Bu)H_4 = *N*,*N*′-bis(3,5-di-*tert*-butyl-2-hydroxybenzyl)-ethylenediamine). In this compound, the imine bonds of the salen(*t*-Bu)H_2 ligand were reduced to form the known ligands salean(*t*-Bu)H_4 and (HO)C_6H_2(*t*-Bu)$_2$CHN(CH_2)$_2$$NH_2$. Compounds **1**, **5**, **6**, and **7** were structurally characterized by single-crystal X-ray diffraction. Crystal data for **1** ($C_{44}H_{74}CaN_2O_6$): triclinic space group $P\bar{1}$, $a = 8.3730(10)$ Å, $b = 14.8010(10)$ Å, $c = 18.756(2)$ Å, $\alpha = 72.551(10)°$, $\beta = 81.795(10)°$, $\gamma = 78.031(10)°$, $Z = 2$. Crystal data for **5** ($C_{38}H_{64}SrN_2O_5$): monoclinic space group $P2_1/c$, $a = 23.634(3)$ Å, $b = 8.4660(10)$ Å, $c = 24.451(3)$ Å, $\beta = 101.138(10)°$, $Z = 4$. Crystal data for **6** ($C_{46}H_{67}N_2O_5Sr$): orthorhombic space group $P2_12_12_1$, $a = 10.5590(2)$ Å, $b = 16.2070(3)$ Å, $c = 26.7620(6)$ Å, $Z = 4$. Crystal data for **7** ($C_{98}H_{156}N_8O_8Sr_4$): triclinic space group $P\bar{1}$, $a = 14.667(1)$ Å, $b = 15.670(1)$ Å, $c = 18.594(2)$ Å, $\alpha = 92.26(1)°$, $\beta = 111.84(1)°$, $\gamma = 117.12(1)°$, $Z = 4$.

Introduction

The chemistry of the salen ligands with transition metals has been extensively explored. However, among main-group metals, only compounds of the Group 13 elements[1] have been studied in much detail.[2] While there are examples of salen ligands coordinated to Group 2 metals through the lone pairs on the oxygen atoms, such as in [Ca(salpenH_2)(NO_3)$_2$],[3] [{Ni(salen)}$_2$Ba(ClO_4)$_2$(thf)],[4] [BaFe(cr-salen)(MeOH)$_2$]$_2$O(ClO_4)$_4$·2MeOH,[5] and Ba(hfa)$_2$(Ni(salen))$_2$,[6] only one structurally characterized example of a Group 2 metal covalently bound to a salen ligand has been reported, [{Mg(acen)}$_2$] (acenH_2= *N*,*N*′-ethylenebis(salicylidene(methyl)imine).[7] The results presented herein describe efforts to explore the synthesis and structural characterization of covalently bound salen compounds of the heavier Group 2 metals, calcium and strontium. Seven new calcium and strontium compounds, [Ca(salen(*t*-Bu))(HOEt)$_2$(thf)] (**1**), [Ca(salen(*t*-Bu))(HOEt)$_2$] (**2**), [Ca(salpen(*t*-Bu))(HOEt)$_3$] (**3**), [Ca(salophen(*t*-Bu))(HOEt)(thf)] (**4**), [Sr(salen(*t*-Bu))(HOEt)$_3$] (**5**), [Sr(salophen(*t*-Bu))(HOEt)(thf)$_2$] (**6**), and [{OC_6H_2(*t*-Bu)$_2$CHN(CH_2)$_2$$NH_2$}Sr($\mu_3$-salean(*t*-Bu)$H_2$)Sr($\mu_3$-OH)]$_2$ (**7**), have been synthesized with the tetradentate Schiff-base ligands salen(*t*-Bu)H_2, salpen(*t*-Bu)H_2, and salophen(*t*-Bu)H_2. The novel structures and bonding in these compounds will be described.

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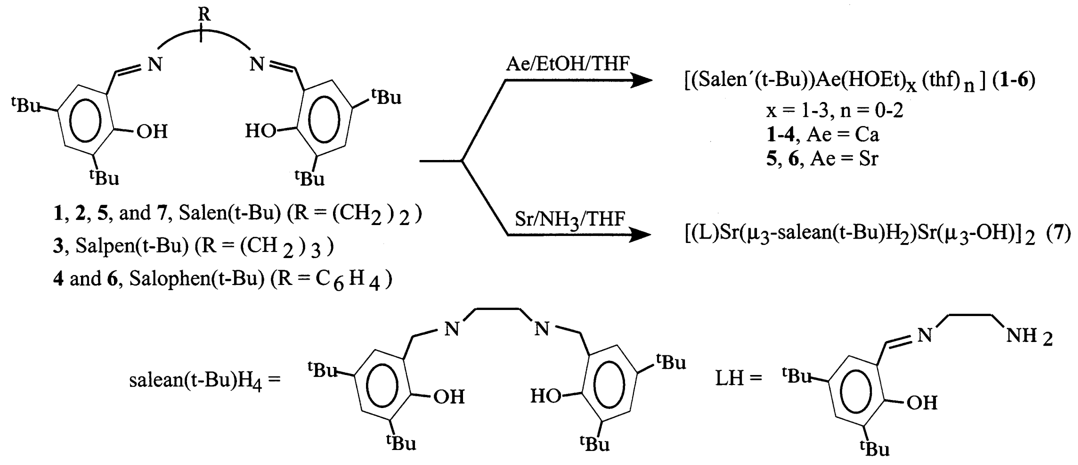
Scheme 1. General Reactions for the Syntheses of Compounds **1**−**7**



Results and Discussion

Synthesis of [Ae(salen(*t*-Bu))(HOEt)$_x$(thf)$_n$]. The ethoxides of the Group 2 metals have been used to form a variety of chelated calcium, strontium, and barium compounds, particularly in the search for useful MOCVD precursors.[8] Compounds of the type [Ae(L(*t*-Bu))(HOEt)$_n$] (Ae = Ca (**2** and **3**), Sr (**5**)) were prepared by the reaction of salen(*t*-Bu)H_2 with calcium or strontium metal in ethanol. Compounds of the type [Ae(L(*t*-Bu))(HOEt)$_n$(thf)$_x$] (Ae = Ca (**1** and **4**), Sr (**6**)) were prepared by the reaction of salen(*t*-Bu)H_2 with calcium or strontium metal in a mixture of ethanol and THF (Scheme 1). The use of THF prevented precipitation of the ligand when it was introduced to the −30 °C ethanol solution. It had the added effect of allowing an exploration into what type of coordination environment would result for Ca with two solvents present. Indeed, the two solvents did compete to coordinate to the metal centers. This is most evident in the structure of **1** (discussed later) in which one of the coordination sites is partially occupied by ethanol and partially by a thf molecule. Preference for one solvent over the other was not evident. Rather, a subtle mix of the two donors occurred giving both six- and seven-coordinate geometries for Ca and only seven-coordinate for Sr.

Compounds **1**−**5** are soluble in polar solvents, and compound **6** is soluble in aromatics. These compounds are all highly air- and moisture-sensitive. When synthesized in the presence of THF, these compounds coordinate both THF and ethanol (compounds **1**, **4**, and **6**). The ^{1}H NMR spectra for these compounds showed signals appearing more deshielded than the corresponding resonances for the free ligands.[9] The resonances for the methine protons of the salen ligands (CH═N) are between 8.18 and 7.98 ppm. Also, the resonances of the OH protons of the ethanol molecules are between 2.84 and 2.71 ppm (free ethanol $\delta \sim 4.3$ ppm). This shielding effect indicates that hydrogen bonding is taking place. Because of the N−M intramolecular coordination, the absorptions in the infrared spectra attributed to the $\nu_{C=N}$ stretching frequency (1624−1611 cm^{-1}) are shifted toward higher frequencies by 4−13 cm^{-1} in comparison with those for the free ligands. This is due to the change in hybridization (s character) at the nitrogen atom upon coordination.[9]

Synthesis of [{OC_6H_2(*t*-Bu)$_2$CHN$(CH_2)_2NH_2$}Sr(μ_3-salean(*t*-Bu)H_2)Sr(μ_3-OH)]$_2$. It is well-known that both the alkali and alkaline-earth metals (with the exception of Li and Mg) readily dissolve and undergo reactions in liquid ammonia. When accompanied by the addition of a desired ligand, these solutions have been used to form a variety of alkali and alkaline-earth metal complexes.[10] However, there have been only a limited number of reports[11] combining these solutions with chelating ligands. Initially, we explored this route for the formation of salen compounds of calcium and strontium. An unusual tetrametallic compound, [{OC_6H_2(*t*-Bu)$_2$CHN$(CH_2)_2NH_2$}Sr(μ_3-salean(*t*-Bu)H_2)Sr(μ_3-OH)]$_2$ (**7**), was isolated from the reaction of salen(*t*-Bu)H_2 with strontium metal in liquid ammonia and THF in high yield (79%) (Scheme 1). In this compound, the imine bonds of the salen(*t*-Bu)H_2 ligand were reduced to form the known ligands salean(*t*-Bu),[12] and one imine bond cleaved to form (HO)C_6H_2(*t*-Bu)$_2$CHN$(CH_2)_2NH_2$ which is a component of **7**. There is precedence for this reduction; group 2 metals in liquid ammonia have been demonstrated to be selective reducing agents for various organic compounds.[13] From the presence of the hydroxyl ligands, the compound was also apparently hydrolyzed. Hydrolysis of one imine bond in a ligand with multiple Schiff-base linkages is known. This was conjectured to occur, in at least two instances, through a zinc-mediated generation of an OH group.[14] Thus, strongly elec-

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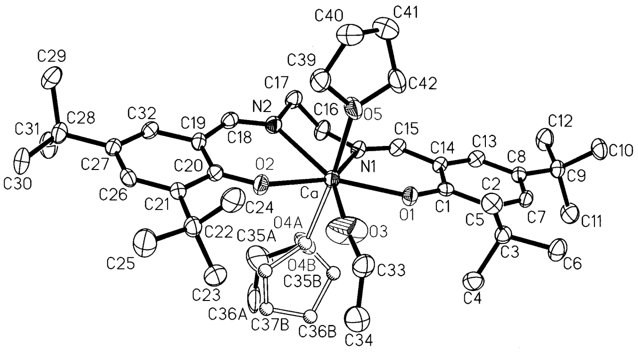

Figure 1. Molecular structure of [Ca(salen(*t*-Bu))(HOEt)$_{1.6}$(thf)$_{1.4}$] (**1**). Hydrogen atoms and disordered lattice solvent are omitted for clarity.

trophilic metals such as Sr and Zn appear capable of causing this salen-degradation reaction, although Cu, as noted in the previous reports, does not.

Solid State Structures. [Ca(salen(*t*-Bu))(HOEt)$_2$(thf)]. Compound **1** crystallizes as a monomer with a salen(*t*-Bu) ligand bound in a tetradentate fashion to a seven-coordinate pentagonal bipyramidal calcium atom (Ca−O(1), 2.280(2) Å; Ca−O(2), 2.309(2) Å; Ca−N(1), 2.518(3) Å; Ca−N(2), 2.512(3) Å) (Figure 1). The calcium atom is coordinated by one thf molecule (Ca−O(5), 2.390(2) Å) and one ethanol molecule (Ca−O(3), 2.399(3) Å), and the last site is occupied partially by ethanol and partially by thf (Ca−O(4a,b), 2.391(2) Å).[15] The apical positions of the pentagonal bipyramid of the calcium atom are occupied by O(4) and O(5). The Ca−O (average 2.30 Å) bond distances in compound **1** are longer than the analogous distance observed in [(C$_5$Me$_5$)Ca(O-2,6-*i*PrC$_6$H$_3$)(thf)$_3$] (2.177(2) Å, Ca−O(aryloxide)).[16] This may be due to the difference in the number of charged oxygen atoms bound to the calcium metal center in each compound. As if to compensate, the O(thf)−Ca distance in compound **1** (Ca−O(5), 2.390(2) Å) is shorter than the analogous distances in [(C$_5$Me$_5$)Ca(O-2,6-*i*PrC$_6$H$_3$)(thf)$_3$] (2.466(3), 2.408(3), 2.454(2) Å).[16] Additionally, the N−Ca (av 2.52 Å) and O(ethanol)−Ca (Ca−O(3), 2.399(3) Å) bond distances in compound **1** are significantly shorter than those previously reported for another compound with seven-coordinate calcium atoms, [Ca$_2$(tmhd)$_4$(OAr$_N$)$_4$(EtOH)$_2$] (HOAr$_N$ = 2,6-*N*,*N*-dimethylaminomethyl-4-methylphenol) (N−Ca, 2.706(4)−2.746(4) Å; O(ethanol)−Ca, 2.482(4) and 2.462(4) Å).[17]

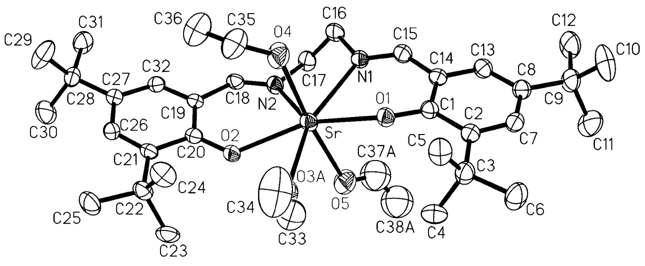

Figure 2. Molecular structure of [Sr(salen(*t*-Bu))(HOEt)$_3$] (**5**). Hydrogen atoms and disordered lattice solvent are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compounds **1**, **5**, **6**, and **7**

[Salen(*t*-Bu)Ca(HOEt)$_2$(thf)] (**1**)			
Ca−O(1)	2.280(2)	Ca−O(2)	2.309(2)
Ca−O(5)	2.390(2)	Ca−O(4A)	2.391(2)
Ca−O(3)	2.399(3)	Ca−N(2)	2.512(3)
Ca−N(1)	2.518(3)	N(2)−Ca−N(1)	68.66(8)
O(1)−Ca−O(2)	148.50(8)	O(1)−Ca−O(5)	88.94(8)
O(2)−Ca−O(5)	88.79(8)	O(1)−Ca−O(4A)[a]	95.90(8)
O(2)−Ca−O(4A)[a]	87.40(8)	O(5)−Ca−O(4A)[a]	175.13(8)
O(1)−Ca−O(3)	77.83(10)	O(2)−Ca−O(3)	70.78(10)
O(5)−Ca−O(3)	90.42(10)	O(1)−Ca−N(1)	71.79(8)
		O(2)−Ca−N(2)	72.34(8)
[Salen(*t*-Bu)Sr(HOEt)$_3$] (**5**)			
Sr−O(1)	2.474(3)	Sr−O(2)	2.487(3)
Sr−O(5)	2.546(4)	Sr−O(4)	2.552(4)
Sr−O(3A)[a]	2.555(7)	Sr−N(1)	2.629(4)
Sr−N(2)	2.629(4)	O(1)−Sr−O(5)	86.70(13)
O(1)−Sr−O(2)	155.62(10)	O(2)−Sr−O(4)	95.19(11)
O(2)−Sr−O(5)	90.55(12)	O(5)−Sr−O(4)	174.10(13)
O(1)−Sr−O(4)	87.50(12)	O(1)−Sr−N(2)	135.07(11)
O(1)−Sr−O(3A)[a]	87.9(2)	O(1)−Sr−N(1)	69.21(11)
O(4)−Sr−O(3A)[a]	95.7(2)	O(2)−Sr−N(2)	69.09(11)
		N(1)−Sr−N(2)	66.07 (12)
[Salophen(*t*-Bu)Sr(HOEt)(thf)$_2$] (**6**)			
Sr−O(1)	2.370(3)	Sr−N(1)	2.648(3)
Sr−O(4)	2.610(8))	Sr−O(2)	2.409(3)
Sr−O(5)	2.623(3)	Sr−O(3)	2.594(3)
Sr−N(2)	2.618(3)	O(1)−Sr−O(2)	111.77(10)
N(2)−Sr−N(1)	61.92(10)	O(1)−Sr−O(4)	86.3(2)
N(1)−Sr−O(3)	158.48(16)	O(2)−Sr−O(5)	84.65(11)
N(2)−Sr−O(5)	81.34(10)	O(2)−Sr−O(3)	69.81(15)
[{C$_6$H$_2$(*t*-Bu)$_2$N(CH$_2$)NH$_2$}Sr(μ-salean(*t*-Bu))Sr(μ-OH)]$_2$ (**7**)			
Sr(1)−O(1)	2.430(3)	Sr(1)−N(2)	2.692(3)
Sr(1)−O(4)	2.441(3)	Sr(2)−N(4)	2.728(4)
Sr(1)−O(2)	2.515(3)	Sr(2)−O(4)	2.512(2)
Sr(1)−N(1)	2.775(3)	Sr(2)−N(3)	2.646(3)
Sr(2)−O(3)	2.376(3)	Sr(2)−O(2A)	2.458(3)
Sr(2)−O(1)	2.517(3)	Sr(1)−O(4)	2.441(3)
O(1)−Sr(1)−O(4)	78.40(8)	O(1)−Sr(1)−O(2)	152.05(9)
O(4)−Sr(1)−O(2)	117.66(9)	O(4)−Sr(1)−N(2)	87.35(9)
O(1)−Sr(1)−N(2)	131.33(10)	O(4)−Sr(1)−N(1)	100.61(9)
O(3)−Sr(2)−O(4)	83.70(9)	O(2)−Sr(1)−N(1)	123.09(9)
O(4)−Sr(2)−O(1)	75.49(8)	N(2)−Sr(1)−N(1)	66.27(10)

[a] Atoms labeled "A" are minor disorder components.

[Sr(salen(*t*-Bu))(HOEt)$_3$]. Compound **5** crystallizes monomeric with a seven-coordinate strontium atom in a distorted pentagonal bipyramidal geometry (Figure 2). The salen(*t*-Bu) ligand and one ethanol molecule occupy the basal plane [Sr−O(1), 2.474(3) Å; Sr−N(1), 2.629(4) Å; Sr−N(2), 2.629(4) Å; Sr−O(2), 2.487(3) Å; Sr−O(3A), 2.555(7) Å], and the axial positions are occupied by two ethanol molecules [Sr−O(4), 2.552(4) Å; Sr−O(5), 2.546(4) Å]. There are two additional ethanol molecules in the lattice. The average values for Sr−O (2.48 Å), N−Sr (2.63 Å), and O−Sr (2.55 Å) bond distances in compound **5** can be compared to the analogous bond lengths for compound **6** (see Table 1). The Sr−O and Sr−N bond distances are significantly longer in **5** than those observed between the seven-coordinate strontium atom and salophen(*t*-Bu) ligand in compound **6** (see Table 1). This is probably due to the resonance stabilization associated with the aromatic backbone. This resonance has been previously noted as a reason certain salophen(tBu)

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(15) The coordinated solvent molecule containing O(4) refined with an occupancy of ~0.6 ethanol and ~0.4 thf. There is also disordered solvent in the lattice that is most likely part thf and part ethanol.

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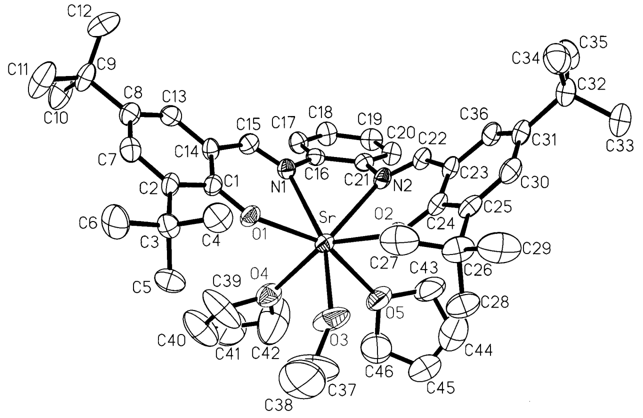


Figure 3. Molecular structure of [Sr(salophen(*t*-Bu))(HOEt)(thf)$_2$] (**6**). Hydrogen atoms and disordered lattice solvent are omitted for clarity.

compounds are able to undergo THF coupling reactions, while the compounds containing salen(tBu) ligands with aliphatic backbones did not.[18] A second consideration is that the N−Sr−N angle in **5** (∼66) is more broad than for **6** (∼62), indicating a slightly less crowded environment for the ligand in **6**. In turn, the Sr−O distances with the ethanol molecules in compound **5** are shorter than those for compound **6** (see Table 1). This observation supports a previous suggestion that heavy alkaline-earth metals are highly sensitive to small electronic changes causing bond distances of the various ligands coordinated to a single alkaline-earth metal center to adjust themselves accordingly.[19] This sensitivity to electronic changes is an interesting feature not commonly observed. For example, there are no significant differences in the Group 13 metal−salen ligand M−O and M−N bond lengths among hydrocarbon and aromatic backbones.[1]

[Sr(salophen(*t*-Bu))(HOEt)(thf)$_2$]. Compound **6** crystallizes monomeric with a central seven-coordinate pentagonal bipyramidal strontium atom coordinated by a tetradentate salophen(*t*-Bu), one ethanol molecule, and two thf molecules (Figure 3). As mentioned earlier and explained in the discussion of compound **5**, the Sr−O (Sr−O(1), 2.370(3) Å; Sr−O(2), 2.409(3) Å) and Sr−N (Sr−N(1), 2.648(3) Å; Sr−N(2), 2.618(3) Å) bond distances are significantly shorter in **6** than those observed between the seven-coordinate strontium atom and salen(*t*-Bu) ligand in compound **5** (see Table 1). As a result, the Sr−O distances with the ethanol molecules (Sr−O(3), 2.594(3) Å; Sr−O(3)′, 2.585(9) Å) are longer than those for compound **6** (av Sr−O(EtOH), 2.55 Å) (see Table 1), and the Sr−O distances with the thf molecules (Sr−O(4), 2.610(8) Å; Sr−O(4)′, 2.618(9) Å; Sr−O(5), 2.623(3) Å) are longer than those in another seven-coordinate strontium compound, {[C$_5$(SiMe$_3$)$_3$H$_2$]SrI(thf)$_2$}$_2$ (2.537(5) Å and 2.558(5) Å).[20]

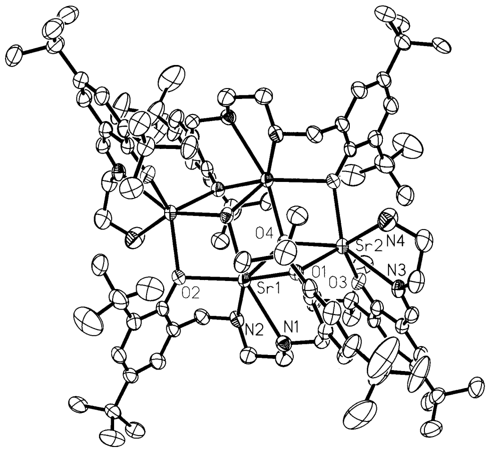
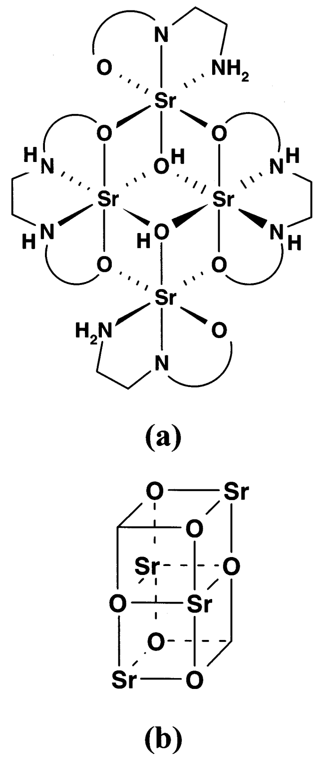


Figure 4. Molecular structure of [{OC$_6$H$_2$(*t*-Bu)$_2$CHN(CH$_2$)$_2$NH$_2$}Sr(μ_3-salean(*t*-Bu)H$_2$)Sr(μ_3-OH)]$_2$ (**7**). Hydrogen atoms and the *t*-Bu groups have been omitted for clarity.



(a)

(b)

Figure 5. (a) Simplified drawing of [{OC$_6$H$_2$(*t*-Bu)$_2$CHN(CH$_2$)$_2$NH$_2$}Sr(μ_3-salean(*t*-Bu)H$_2$)Sr(μ_3-OH)]$_2$ (**7**). (b) Drawing of the “dicubane-like” Sr$_4$O$_6$ core.

[{OC$_6$H$_2$(*t*-Bu)$_2$CHN(CH$_2$)$_2$NH$_2$}Sr(μ_3-salean(*t*-Bu)H$_2$)Sr(μ_3-OH)]$_2$. Compound **7** crystallizes as a tetrametallic cluster (Figure 4). The oxygen and strontium atoms form a “dicubane-like tetramer” (Figure 5) similar to that observed in the structure of [Mg$_4$(thf)$_6$(OSiPh$_3$)$_2$].[21] More specifically, the four Sr atoms may be described as being located at the four corners of a defective double cubane which results from two cubanes sharing one face and missing one vertex. Compound **7** sits on an inversion center making only half of the molecule unique. The four six-coordinate strontium

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Table 2. Crystallographic Data

	[Ca(salen(*t*-Bu))(HOEt)$_2$(thf)] (**1**)	[Sr(salen(*t*-Bu))(HOEt)$_3$] (**5**)	[Sr(Salophen(*t*-Bu))(HOEt)(thf)$_2$] (**6**)	[{OC$_6$H$_2$(*t*-Bu)$_2$CHN(CH$_2$)$_2$NH$_2$}Sr(μ_3-salean(*t*-Bu)H$_2$)Sr(μ_3-OH)]$_2$ (**7**)
formula	$C_{44}H_{74}CaN_2O_6$	$C_{38}H_{64}SrN_2O_5$	$C_{46}H_{67}N_2O_5Sr$	$C_{98}H_{156}N_8O_8Sr_4$
fw	767.16	716.55	815.64	1924.84
cryst syst, space group	triclinic, $P\bar{1}$	monoclinic, $P2_1/c$	orthorhombic, $P2_12_12_1$	triclinic, $P\bar{1}$
T (K)	173(1)	205(1)	173(1)	144(1)
a (Å)	8.3730(10)	23.634(3)	10.5590(2)	14.667(1)
b (Å)	14.8010(10)	8.4660(10)	16.2070(3)	15.670(1)
c (Å)	18.756(2)	24.451(3)	26.7620(6)	18.594(2)
α (deg)	72.551(10)			92.26(1)
β (deg)	81.795(10)	101.138(10)		111.84(1)
γ (deg)	78.031(10)			117.12(1)
V (Å^3)	2161.2(4)	4800.1(10)	4579.77(16)	3415.7(4)
Z	2	4	4	4
abs coeff	0.188 mm^{-1}	1.166 mm^{-1}	1.220 mm^{-1}	1.609 mm^{-1}
D (calcd)	1.126 Mg/m^3	1.112 Mg/m^3	1.183 Mg/m^3	1.204 Mg/m^3
final R indices	R1 = 0.0549	R1 = 0.0683	R1 = 0.0539	R1 = 0.0540
[$I > 2\sigma(I)$]	wR2 = 0.1253	wR2 = 0.1621	wR2 = 0.0982	wR2 = 0.1189
R indices (all data)	R1 = 0.0842	R1 = 0.1000	R1 = 0.0734	R1 = 0.0898
	wR2 = 0.1368	wR2 = 0.1756	wR2 = 0.1046	wR2 = 0.1332

atoms are bridged by two hydroxide groups (Sr(1)−O(4), 2.441(3) Å; Sr(2)−O(4), 2.512(2) Å). One pair of strontium atoms are each bound to a terminal tridentate salen(*t*-Bu) fragment (Sr(2)−O(3), 2.376(3) Å; Sr(2)−N(3), 2.646(3) Å; Sr(2)−N(4), 2.728(4) Å), and the other pair are each bound by a tetradentate salean(*t*-Bu) ligand (Sr(1)−O(1), 2.430(3) Å; Sr(1)−O(2), 2.515(3) Å; Sr(1)−N(1), 2.775(3) Å; Sr(1)−N(2), 2.692(3) Å). The oxygen atoms of the salean(*t*-Bu) ligands also form a bridging interaction with the other pair of strontium atoms (Sr(2)−O(1), 2.517(3) Å; Sr(2)−O(2), 2.458(3) Å). A deliberate hydrolysis of a salen compound of lithium formed, [(salen)Li$_2$]$_3$•Li$_2$O•2tmen•H$_2$O, whose structural core similarly exhibited two distorted Li$_4$O$_4$ cubes joined by one common oxygen.[22]

Conclusion

A series of salen complexes of the heavy alkaline-earth metals, calcium and strontium, has been reported. Although alkaline-earth metal and ammonia solutions reduced the salen ligands, the addition of a small amount of ammonia to Group 2 metal−ethanol solutions was found to harmlessly speed reactions with salen ligands. The structures of compounds **5** and **6** demonstrate the high sensitivity of these large electrophilic metals to slight changes in electronic donation from ligands. The solvent ligands adjusted themselves as if to compensate for the shortening of the Group 2 metal−salen M−O and M−N bonds.

Experimental Section

All reactions were carried out in an inert atmosphere (nitrogen-filled drybox). Solvents (THF and toluene) were rigorously dried prior to use and dispensed in the drybox. Ethanol anhydrous, calcium metal, and strontium metal were used as received (Aldrich). IR spectra were recorded as KBr pellets on a MAGNA-IR 560 spectrometer. ^{1}H NMR spectra were obtained on a Varian 200 spectrometer. Chemical shifts were reported relative to SiMe$_4$ and are in ppm. Elemental analyses were obtained on a Elementar Americas Vario EL III analyzer. X-ray data were collected on a Nonius Kappa CCD unit ($\lambda_{\mathrm{MoK}\alpha}$ = 0.71073 Å, monochromator: graphite, T = 173 K, $\omega-2\theta$ scan). The scaling and merging routine in Scalepack[21] provided for correction of absorption effects. Direct methods (SHELXS-97) were used for structure solution, and a riding model software package (SHELXL-97) was used for refinement and data output. Hydrogen atoms were refined with isotropic U tied to their respective heavy atom. Further details of the structure analyses are given in Table 2. Selected bond lengths and angles are given in Table 1.

[Ca(salen(*t*-Bu))(HOEt)$_2$(thf)] (1). To a flask with calcium metal (0.05 g, 1.25 mmol) dissolved in ethanol (30 mL) and liquid ammonia (3 mL) at −33 °C was added a solution of *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)ethylenediamine (salen(*t*-Bu)H$_2$) (0.50 g, 1.01 mmol) in THF (30 mL). The reaction was refluxed for 3 h, filtered, and stored at −10 °C. After 24 h in the freezer, 0.61 g (78% yield) of pale yellow air- and moisture-sensitive crystals formed. Mp 110−112 °C. ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 8.08 (2H, s, N═C*H*), 7.28 (2H, d, ring-*H*), 6.90 (2H, d, ring-*H*), 3.68 (4H, m, C*H*$_2$−N), 3.68 (8H, m, α-C$_4$H$_8$O), 3.40 (4H, br, CH$_3$C*H*$_2$OH), 2.70 (2H, br, CH$_3$CH$_2$O*H*), 1.77 (8H, m, β-C$_4$H$_8$O), 1.42 (18H, s, CC*H*$_3$), 1.25 (18H, s, CC*H*$_3$), 1.16 (6H, t, C*H*$_3$CH$_2$-OH). IR (KBr): ν = 3420w, 2953s, 2880m, 1620s, 1541m, 1524m, 1437s, 1336m, 1253m, 1155m, 1045m cm^{-1}. Suitable elemental analysis could not be obtained because of the high sensitivity of the compound toward air and moisture.

[Ca(salen(*t*-Bu))(HOEt)$_2$] (2). To a flask with calcium metal (0.05 g, 1.25 mmol) dissolved in ethanol (30 mL) and liquid ammonia (3 mL) at −33 °C was added a solution of *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)ethylenediamine (salen(*t*-Bu)H$_2$) (0.50 g, 1.01 mmol) in ethanol (30 mL). The reaction was refluxed for 3 h and filtered, and the solvent was removed under reduced pressure, yielding 0.50 g (79% yield) of a pale yellow air- and moisture-sensitive powder. Mp 123−125 °C. ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 8.18 (2H, s, N═C*H*), 7.36 (2H, d, ring-*H*), 7.00 (2H, s, ring-*H*), 3.67 (4H, m, CH$_3$C*H*$_2$−OH), 3.53 (4H, s, C*H*$_2$−N), 2.84 (2H, br, CH$_3$CH$_2$O*H*), 1.48 (18H, s, CC*H*$_3$), 1.31 (18H, s, CC*H*$_3$), 1.14 (6H, t, C*H*$_3$CH$_2$OH). IR (KBr): ν = 3673w, 2959s, 2905m, 2867m, 1624s, 1527m, 1464m, 1437m, 1410m, 1390m, 1361m, 1270m, 1254m, 1233m, 1158m, 1042m cm^{-1}. Calcd: C, 69.41; H, 9.38; N, 4.49. Found: C, 71.09; H, 9.71; N, 4.82.

[Ca(salpen(*t*-Bu))(HOEt)$_3$] (3). To a flask with calcium metal (0.04 g, 1.05 mmol) dissolved in ethanol (30 mL) and liquid ammonia (3 mL) at −33 °C was added a solution of *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,3-propanediamine (salpen(*t*-Bu)H$_2$) (0.50 g, 0.99 mmol) in ethanol (30 mL). The reaction was refluxed for 3 h and filtered, and the solvent was removed under reduced pressure, yielding 0.49 g (73% yield) of a pale yellow air- and moisture-sensitive powder. Mp 206−208 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.98 (2H, s, N=C*H*), 7.28 (2H, s, ring-*H*), 6.89 (2H, s, ring-*H*), 3.59 (6H, m, CH_3CH_2OH), 3.46 (4H, br, CH_2−N), 1.93 (3H, br, CH_3CH_2OH), 1.80 (2H, m, CH_2CH_2−N), 1.35 (18H, s, CCH_3), 1.24 (18H, s, CCH_3), 1.13 (9H, t, CH_3CH_2OH). IR (KBr): ν = 3649w, 3629w, 2557s, 2866m, 1615s, 1540m, 1521m, 1460m, 1438s, 1412m, 1384m, 1359m, 1255m, 1160m, 1114w, 1058m cm^{-1}. Suitable elemental analysis could not be obtained because of the high sensitivity of the compound toward air and moisture.

[Ca(salophen(*t*-Bu))(HOEt)(thf)] (4). To a flask with calcium metal (0.04 g, 1.00 mmol) dissolved in ethanol (30 mL) and liquid ammonia (3 mL) at −33 °C was added a solution of *N*,*N*′-*o*-phenylenebis(3,5-di-*tert*-butylsalicylideneimine) (salophen(*t*-Bu)-H_2) (0.5 g, 0.92 mmol) in THF (30 mL). The reaction was refluxed for 3 h and filtered, and the solvent was removed under reduced pressure, yielding 0.53 g (82% yield) of a pale yellow air- and moisture-sensitive powder. Mp 223−225 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.00 (2H, s, N=C*H*), 7.17 (2H, m, ring-*H*), 7.03 (4H, m, ring-*H*), 6.74 (2H, s, ring-*H*), 3.74 (2H, s, CH_2−O), 3.64 (4H, m, α-C_4H_8O), 2.21 (1H, br, CH_3CH_2OH), 1.73 (4H, m, β-C_4H_8O), 1.34 (18H, s, CCH_3), 1.15 (18H, s, CCH_3), 1.15 (3H, s, CH_3CH_2OH). IR (KBr): ν = 3747w, 3673w, 3649w, 2957s, 2959s, 2904m, 1611s, 1575s, 1522s, 1460m, 1435m, 1387w, 1258m, 1156m, 1104w, 1023w cm^{-1}. Suitable elemental analysis could not be obtained because of the high sensitivity of the compound toward air and moisture.

[Sr(salen(*t*-Bu))(HOEt)$_3$] (5). To a flask with strontium metal (0.10 g, 1.14 mmol) dissolved in ethanol (30 mL) and liquid ammonia (3 mL) at −33 °C was added a solution of *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)ethylenediamine (salen(*t*-Bu)H_2) (0.50 g, 1.01 mmol) in ethanol (30 mL). The reaction was refluxed for 3 h, filtered, and stored at −10 °C. After 24 h in the freezer, 0.67 g (92% yield) of pale yellow air- and moisture-sensitive crystals formed. Mp 70−72 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.14 (2H, s, N=C*H*), 7.27 (2H, d, ring-*H*), 6.90 (2H, d, ring-*H*), 3.63 (4H, s, CH_2−N), 3.60 (10H, q, CH_3CH_2OH), 2.55 (5H, br, CH_3CH_2OH), 1.44 (18H, s, CCH_3), 1.26 (18H, s, CCH_3), 1.12 (15H, t, CH_3CH_2OH). IR (KBr): ν = 3420w, 2953s, 2880m, 1620s, 1541m, 1524m, 1437s, 1336m, 1253m, 1155m, 1045m cm^{-1}. Calcd: C, 63.69; H, 9.00; N, 3.90. Found: C, 64.78; H, 8.58; N, 3.61.

[Sr(salophen(*t*-Bu))(HOEt)(thf)$_2$] (6). To a flask with strontium metal (0.16 g, 1.85 mmol) dissolved in ethanol (30 mL) and liquid ammonia (15 mL) at −33 °C was added a solution of *N*,*N*′-*o*-phenylenebis(3,5-di-*tert*-butylsalicylideneimine) (salophen(*t*-Bu)-H_2) (1.00 g, 1.85 mmol) in THF (30 mL). The reaction was refluxed for 4 h, filtered, and stored at room temperature. After 24 h in the freezer, 1.01 g (71% yield) of pale yellow air- and moisture-sensitive crystals formed. Mp >400 °C. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 7.13−7.00 (8H, m, ring-*H*), 3.57 (8H, m, α-C_4H_8O), 3.30 (6H, m, CH_3CH_2OH, CH_3CH_2OH), 1.41 (8H, m, β-C_4H_8O), 1.23 (18H, s, CCH_3), 0.89 (18H, s, CCH_3), 0.89 (6H, m, CH_3CH_2OH). IR (KBr): ν = 3447w, 2956s, 2870m, 1694w, 1645s, 1569m, 1518s, 1465s, 1436m, 1386w, 1258w, 1154m, 1047w cm^{-1}. Suitable elemental analysis could not be obtained because of the high sensitivity of the compound toward air and moisture.

[{OC_6H_2(*t*-Bu)$_2$CHN(CH_2)$_2$$NH_2$}Sr($\mu_3$-salean(*t*-Bu)$H_2$)Sr($\mu_3$-OH)]$_2$ (7). To a flask with strontium metal (0.21 g, 2.4 mmol) dissolved in liquid ammonia (50 mL) at −33 °C was added a solution of *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)ethylenediamine (salen(*t*-Bu)H_2) (1.00 g, 2.03 mmol) in THF (50 mL). A precipitate immediately formed, and the cloudy mixture was allowed to stir and warm to room temperature overnight. The yellow solid was isolated by filtration, dissolved in toluene, and stored at −10 °C. After 3 days in the freezer, 0.95 g (79% yield) of pale yellow crystals formed. Mp 246−249 °C. IR(KBr): ν = 3490w, 2959s, 1653m, 1623m, 1576m, 1558m, 1539m, 1506m, 1472s, 1436s, 1411m, 1360m, 1299m, 1234m, 1153w. ^{1}H NMR could not be obtained because of the insoluble nature of the compound. Calcd: C, 61.15; H, 8.16; N, 3.90. Found: C, 60.52; H, 8.28; N, 3.61.

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