

# Synthesis and Characterization of the Strontium Thiolate $\text{Sr}(\text{SMes}^*)_2(\text{THF})_4 \cdot 2\text{THF}$ ( $\text{Mes}^* = 2,4,6\text{-tBu}_3\text{C}_6\text{H}_2$ ) and Selenolate $\text{Sr}(\text{SeMes}^*)_2(\text{THF})_4 \cdot 2\text{THF}$ . Structural Investigation of $\text{SrI}_2(\text{THF})_5$

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The syntheses and structural characterization of the strontium thiolate  $\text{Sr}(\text{SMes}^*)_2(\text{THF})_4 \cdot 2\text{THF}$ , **1** ( $\text{Mes}^* = 2,4,6\text{-tBu}_3\text{C}_6\text{H}_2$ ), and selenolate  $\text{Sr}(\text{SeMes}^*)_2(\text{THF})_4 \cdot 2\text{THF}$ , **2**, are described. We also report the synthesis and structural characterization of  $\text{SrI}_2(\text{THF})_5$ , **3**, the apparent starting material for the synthesis of **1** and **2**. **3** exhibits pentagonal bipyramidal geometry at the strontium atom. **3** can be prepared by dissolving  $\text{SrI}_2$  in THF, while the treatment of **3** with 2 equiv of the sterically demanding potassium thiolate and selenolate in THF affords **1** and **2** in good yields. **1** and **2** exhibit distorted octahedral environments at the metal center, with the degree of distortion much more significant for the thiolato derivative. **1** and **2** were characterized by  $^1\text{H}$  NMR and IR spectroscopy, elemental analysis, and X-ray crystallography; **3** was characterized by single-crystal structure analysis. Crystal data with  $\text{Mo K}\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) at 213 K are as follows. **1**:  $a = 18.535(4) \text{ \AA}$ ,  $b = 19.222(4) \text{ \AA}$ ,  $c = 18.775(4) \text{ \AA}$ ,  $\beta = 107.30(3)^\circ$ ,  $V = 6387(2) \text{ \AA}^3$ ,  $Z = 4$ , monoclinic, space group  $I2/a$ , 2254 ( $I > 3\sigma(I)$ ) data,  $R = 0.071$ . **2**:  $a = 18.330(4) \text{ \AA}$ ,  $b = 19.498(4) \text{ \AA}$ ,  $c = 18.608(4) \text{ \AA}$ ,  $\beta = 105.52(3)^\circ$ ,  $V = 6408(3) \text{ \AA}^3$ ,  $Z = 4$ , monoclinic, space group  $I2/a$ , 2331 ( $I > 3\sigma(I)$ ) data,  $R = 0.057$ . **3**:  $a = 8.851(1) \text{ \AA}$ ,  $c = 35.353(7) \text{ \AA}$ ,  $V = 2770(1) \text{ \AA}^3$ ,  $Z = 4$ , tetragonal, space group  $P4_32_1$ , 939 ( $I > 3\sigma(I)$ ) data,  $R = 0.069$ .

## Introduction

In contrast to Mg, whose chemistry is well-developed,<sup>2</sup> the other alkaline-earth elements have received little attention.<sup>3</sup> This might be due to the high toxicity of Be and its compounds<sup>4</sup> but also to the experimental hurdles involved with heavier alkaline-earth elements, making their synthetic access more difficult. These problems involve the high ionic character of the alkaline-earth elements, their large atomic radii, and the low solubility of the dihalide starting materials in organic solvents. Other obstacles relate to the high sensitivity of many alkaline-earth derivatives to hydrolysis as well as their kinetic instability, especially if small groups such as methyl are attached to the metal center.<sup>5,6</sup> As a result, alkaline-earth compounds often polymerize, the products being highly insoluble solids which cannot be subjected to conventional spectroscopic or crystallographic analysis. In addition, the low solubility of the dihalide starting materials requires the use of polar solvents, such as ethers. The kinetic lability causes disproportionation reactions, resulting in complex, difficult to separate product mixtures.

However, the use of sterically demanding ligands allows the synthesis of monomeric or oligomeric alkaline-earth species that

are soluble in organic solvents and therefore accessible to spectroscopic and crystallographic analysis. The use of bulky ligands also increases the kinetic stability of the target molecules, thus facilitating synthetic access to the desired species.

The number of Be species currently structurally characterized is limited to approximately 40 examples, most of which are four-coordinate.<sup>7</sup> There are only a few examples in which Be has a coordination number of 3 or lower.<sup>8</sup> Magnesium compounds are by far the best characterized among group 2 species, but compounds in which Mg is connected to atoms other than C, N, or O are rare.<sup>9</sup> Well-characterized examples of molecular compounds involving the heavier alkaline-earth elements are even more scarce. Examples reported so far consist of a collection of cyclopentadienyl derivatives, for example  $(\text{Me}_5\text{C}_5)_2\text{M}$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ),<sup>10–12</sup>  $(1,3\text{-tBu}_2\text{H}_2\text{C}_5)_2\text{Ca}(\text{THF})$ ,<sup>13,14</sup> the *ansa* metallocenes  $[\text{Me}_2\text{Et}_2\text{C}_2(\text{C}_5\text{H}_4)_2\text{M}]$  ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ ),<sup>15</sup> bis(peralkylcyclopentadienyl) complexes of Ca and Ba,<sup>16</sup> and

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the mono(tetraisopropylcyclopentadienyl) complex of calcium.<sup>17</sup> Other well-characterized alkaline-earth derivatives include amido derivatives, such as the monomeric  $\text{Be}\{\text{N}(\text{SiMe}_3)_2\}_2$ ,<sup>18,19</sup> the donor-free amido dimers  $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2]$  ( $\text{M} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$ ), and a collection of monomeric etherates.<sup>20–24</sup> Notable also is the monomeric phosphazane complex  $\text{Ca}\{\text{N}[\text{P}(\text{NMe}_2)_2\text{NSiMe}_3]_2\}_2$ .<sup>25</sup> Alkaline-earth alkoxides and aryloxides are fairly well investigated, which is due to the importance of the Ba materials as precursors for the low-temperature fabrication of high-temperature superconductors.<sup>3</sup> Examples of alkaline-earth alkoxides and aryloxides include  $\text{Be}(\text{OMes}^*)_2(\text{OEt}_2)$ ,<sup>8</sup>  $[\text{Mg}\{\text{O}(2,6\text{-tBu}_2\text{C}_6\text{H}_3)\}_2]_2$ ,<sup>26</sup> and the heavier analogues  $\text{Ca}\{\text{O}(2,6\text{-tBu}_2\text{-MeC}_6\text{H}_3)\}(\text{THF})_3$ ,<sup>27</sup>  $\text{Sr}_4(\text{OPh})_8(\text{PhOH})_2(\text{THF})_6$ ,<sup>28</sup>  $\text{Sr}_3(\text{OPh})_6\{\text{OP}(\text{NMe}_2)_3\}_5$ ,<sup>29</sup>  $\text{Ba}_3\{\text{OSiPh}_3\}_6\cdot\text{THF}$ ,<sup>30</sup> and  $\text{Ba}_6(\text{OPh})_{12}\text{-}(\text{TMEDA})_4$ .<sup>29</sup> However, information about alkaline-earth elements connected to heavier atoms from row 2 or row 3 of the periodic table is even more limited. Recently, the syntheses and structural characterizations of the magnesium and calcium tellurolate etherates  $\text{Mg}\{\text{TeSi}(\text{SiMe}_3)_3\}_2(\text{THF})_2$  and  $\text{Ca}\{\text{TeSi}(\text{SiMe}_3)_3\}_2(\text{THF})_4$  were reported.<sup>31</sup> Other examples are  $\text{Ca}\{\text{P}(\text{SiMe}_3)_2\}_2\cdot 2\text{TMTA}$  (TMTA = 1,3,5-trimethyl-1,3,5-triazinane) and  $\text{Ba}\{\text{P}(\text{SiMe}_3)_2\}_2(\text{THF})_4$ .<sup>25</sup> Also recently, we reported the synthesis and structural characterization of the first base-free, three-coordinate magnesium thiolate  $[\text{Mg}\{\text{S}(2,4,6\text{-Ph}_3\text{C}_6\text{H}_2)\}_2]_2$  and the etherates  $\text{Mg}\{\text{S}(2,4,6\text{-tBu}_3\text{C}_6\text{H}_2)\}_2(\text{Et}_2\text{O})_2$  and  $\text{Mg}\{\text{Se}(2,4,6\text{-tBu}_3\text{C}_6\text{H}_2)\}_2(\text{THF})_2$ .<sup>9</sup> This paper describes the synthesis and structural characterization of two strontium derivatives in which Sr is bound to atoms from the second and third rows of the periodic table.  $\text{Sr}(\text{SMes}^*)_2(\text{THF})_4\cdot 2\text{THF}$ , **1**, and  $\text{Sr}(\text{SeMes}^*)_2(\text{THF})_4\cdot 2\text{THF}$ , **2**, display distorted octahedral coordination spheres at the metal center. Also included are the synthesis and structural characterization of  $\text{SrI}_2(\text{THF})_5$ , **3**, the starting material for the synthesis of **1** and **2**.  $\text{SrI}_2(\text{THF})_5$  displays almost perfect pentagonal bipyramidal geometry at the metal center.

During preparation of this work for publication, we became aware of related work, just published by Gindelberger and Arnold, who describe the preparation of a series of Ca, Sr, and Ba selenolates and tellurolates bearing the  $-\text{ESi}(\text{SiMe}_3)_3$  ligand ( $\text{E} = \text{Se}, \text{Te}$ ).<sup>32</sup>

## Experimental Section

**General Procedures.** All reactions were performed under purified nitrogen atmosphere by using either modified Schlenk techniques or a Braun Labmaster 100 drybox. *n*-Hexane and THF were freshly distilled from a Na/K alloy and degassed two times before use. Commercially available  $\text{SrI}_2$ , *n*-BuLi (1.6 M solution in hexanes), and KH (35 wt % dispersion in mineral oil) were used as received. The compounds  $\text{HSMes}^*$ <sup>33</sup> and  $\text{HSeMes}^*$ <sup>34</sup> were synthesized by following literature procedures. <sup>1</sup>H NMR spectra were obtained at 300 MHz in  $\text{C}_6\text{D}_6$  using a GE QE-300 spectrometer. Infrared spectra were recorded as Nujol mulls between KBr plates, using a Perkin-Elmer PE 1600 FT-IR spectrometer.

**Synthesis of  $\text{Sr}(\text{SMes}^*)_2(\text{THF})_4\cdot 2\text{THF}$ , **1**.** A 0.23 g sample of KH (2 mmol, 35 wt % dispersion in mineral oil) was washed twice with hexane to remove the mineral oil. The resulting white powder was suspended in 10 mL of THF, and 0.556 g of  $\text{HSMes}^*$  (2 mmol), dissolved in 20 mL of THF, was added. The reaction proceeded immediately, easily recognized by the formation of hydrogen gas. The resulting pale yellow solution was stirred for 1 h and then added to a solution of 0.341 g of  $\text{SrI}_2$  (1 mmol) dissolved in 30 mL of THF. The reaction mixture was stirred for 18 h, during which it became cloudy. The suspension was filtered through a Celite padded filter frit and the volume of the clear, pale yellow solution reduced to 20 mL. After storage of the solution at  $-20^\circ\text{C}$  for several days, large colorless crystals, suitable for X-ray crystallography were obtained in 72% yield (0.77 g). Mp: dec  $>270^\circ\text{C}$ .  $\delta$ , <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ): 1.40 (s, *p*-tBu, 9H), 1.420 (m, THF, 16H), 1.599 (s, *o*-tBu, 18H), 3.562 (m, THF, 16H), 7.548 (s, *m*-H, 2H). IR ( $\text{cm}^{-1}$ ): 1596 m, 1538 w, 1462 s, 1377 s, 1287 m, 1261 m, 1241 m, 1212 m, 1173 m, 1070 m, 1037 s, 876 s, 756 m, 722 m, 665 m, 640 m, 614 m, 490 w. Anal. Calcd: C, 67.02; H, 9.94. Found: C, 68.72; H, 9.79.

**Synthesis of  $\text{Sr}(\text{SeMes}^*)_2(\text{THF})_4\cdot 2\text{THF}$ , **2**.** A 4.08 mmol amount of KH was prepared in a fashion identical with that described above and suspended in 15 mL of THF. A 1.33 g sample of freshly reduced  $\text{HSeMes}^*$  (4.08 mmol) was dissolved in 20 mL of THF, and the solution was slowly added to the KH suspension. The reaction started immediately, recognizable by the formation of hydrogen gas. The resulting pale yellow solution was stirred for 2 h at room temperature. A 0.7 g amount of  $\text{SrI}_2$  (2.08 mmol) was dissolved in 30 mL of THF, and the potassium selenolate solution was added dropwise via cannula. The solution was stirred overnight, during which it became cloudy. The solids were removed via filtration, and the volume of the clear yellow solution was reduced to 20 mL. After storage of the mother liquor at  $-20^\circ\text{C}$  for a few days, 1.38 g (59%) colorless needle-shaped crystals suitable for X-ray crystallography were isolated. Mp: 120–125  $^\circ\text{C}$ .  $\delta$ , <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ): 1.39 (m, THF and *o*-tBu, 25H), 2.02 (s, *o*-tBu, 18H), 3.55 (m, THF, 16H), 7.55 (s, *m*-H, 2H). IR ( $\text{cm}^{-1}$ ): 1460 s, 1374 m, 1030 w, 1016 w, 871 w. Anal. Calcd: C, 61.65; H, 9.14. Found: C, 60.79; H, 8.98.

**Synthesis of  $\text{SrI}_2(\text{THF})_5$ , **3**.**  $\text{SrI}_2(\text{THF})_5$  is obtained by dissolving  $\text{SrI}_2$  in THF. However, the first crop of this material was obtained after the attempted synthesis of  $\text{Sr}(\text{SMes}^*)_2(\text{THF})_4$  via the reaction of  $\text{SrI}_2$  with 2 equiv of the lithium thiolate at room temperature. A repetition of this experiment in refluxing THF gave the same result.  $\text{SrI}_2(\text{THF})_5$  was easily synthesized by dissolving  $\text{SrI}_2$  in refluxing THF (usually 1 mmol of  $\text{SrI}_2$  in 20 mL of THF), filtration of the slightly cloudy solution, and the careful reduction of the reaction volume. Storage of the solution at room temperature afforded colorless crystals suitable for X-ray crystallography. Upon removal of the crystals from the mother liquor, decomposition was observed, presumably caused by the loss of THF.

**X-ray Crystallographic Studies.** The crystals were removed from the Schlenk tube under a stream of  $\text{N}_2$  and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected, attached to a glass fiber, and immediately placed

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**Table 1.** Summary of Data Collection and Structure Solution and Refinement Parameters for Sr{S(2,4,6-tBu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>(THF)<sub>4</sub>·2THF, **1**, Sr{Se(2,4,6-tBu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>(THF)<sub>4</sub>·2THF, **2**, and SrI<sub>2</sub>(THF)<sub>5</sub>, **3**

	<b>1</b>	<b>2</b>	<b>3</b>
formula	C <sub>60</sub> H <sub>106</sub> O <sub>6</sub> S <sub>2</sub> Sr	C <sub>60</sub> H <sub>106</sub> O <sub>6</sub> Se <sub>2</sub> Sr	C <sub>20</sub> H <sub>40</sub> I <sub>2</sub> O <sub>5</sub> Sr
fw	1075.2	1169.0	701.9
crystal descriptn	colorless plate	colorless needle	colorless plate
<i>a</i> (Å)	18.535(4)	18.330(4)	8.8510(10)
<i>b</i> (Å)	19.222(4)	19.498(4)	
<i>c</i> (Å)	18.775(4)	18.608(4)	35.353(7)
$\beta$ (deg)	107.30(3)	105.52(3)	
<i>V</i> (Å <sup>3</sup> )	6387(2)	6408(3)	2770(1)
<i>Z</i>	4	4	4
space group	<i>I</i> 2/ <i>a</i>	<i>I</i> 2/ <i>a</i>	<i>P</i> 4 <sub>3</sub> 2 <sub>1</sub> 2
<i>d</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.118	1.212	1.683
linear abs coeff (mm <sup>-1</sup> )	0.949	2.017	4.200
radiation	Mo K $\alpha$	Mo K $\alpha$	Mo K $\alpha$
<i>T</i> (K)	213	213	213
2 $\theta$ range (deg)	2–50	2–50	2–45
range of transm factors	0.955–1.0	0.902–1.0	0.892–1.0
no. of obs reflns	2254	2331	939
no. of variables	295	295	127
<i>R</i> , <i>R</i> <sub>w</sub> <sup>b</sup>	0.071, 0.074	0.057, 0.058	0.069, 0.063

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2]^{1/2}.$$

in the low-temperature nitrogen stream of the diffractometer.<sup>35</sup> Compounds **1**–**3** were collected at 213 K using a Rigaku AFC5S diffractometer (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å) equipped with a monochromator and a Molecular Structure Corp. low-temperature device for low-temperature work. Three standard reflections were measured every 150 reflections and showed in all cases only statistical variation of the intensity (<1.5%). The intensities were corrected for Lorentz and polarization effects; extinction was disregarded. An absorption correction (for **1** and **2**) was applied using semiempirical  $\psi$ -scans. In the case of **3**, owing to a weak data set, no suitable reflections for  $\psi$ -scans were found; therefore an absorption correction was disregarded. Crystallographic programs used for the structure solutions and refinement were those of SHELXTL-Plus installed on a PC clone.<sup>36</sup> Scattering factors were those provided with the SHELXTL-Plus program system. Some details of the data collections and refinements are given in Table 1, atomic coordinates of selected atoms are provided in Table 2, and important bond lengths and angles are given in Tables 3 and 4. Further details are provided in the supplementary material.

X-ray-quality crystals for all compounds were grown from concentrated THF solutions. Crystals of **1** and **2** were obtained by slow cooling of the stock solutions to –20 °C using an acetone-filled Dewar flask which was covered with aluminum foil and placed in a freezer. X-ray suitable crystals of **3** were grown at room temperature. The intensity data set of **1** was collected in a monoclinic *C*-centered setting (space group *C*2/*c*), which was subsequently transformed into a monoclinic *I* cell (space group *I*2/*a*) to obtain a smaller  $\beta$  angle. Refinement using the noncentrosymmetric space group *Cc* was attempted but resulted in a model which could not be refined satisfactorily. The data set of **2** was collected in a triclinic setting and was later transformed into a monoclinic *I* cell, analogous to **1**, making them isomorphous.

The crystal structures of **1** and **3** were solved by direct methods; missing atoms were located in the difference Fourier map and included in subsequent refinement cycles. The structure of **2** was solved using the coordinates of **1**. The structures were refined by full-matrix least-squares refinement on  $|F_o|$ . The function minimized was  $\sum w(|F_o| - |F_c|)^2 / w(F)^2$ . In all cases, hydrogen atoms were included using a riding model with C–H distances of 0.96 Å and fixed isotropic thermal parameters of 0.08 Å<sup>2</sup>. Both **1** and **2** contain one THF solvent molecule, which is severely disordered and was included in the refinement using

**Table 2.** Atomic Coordinates ( $\times 10^4$ ) and Isotropic Thermal Parameters (Å<sup>2</sup>  $\times 10^3$ ) for Significant Atoms in Sr{S(2,4,6-tBu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>(THF)<sub>4</sub>·2THF, **1**, Sr{Se(2,4,6-tBu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>(THF)<sub>4</sub>·2THF, **2**, and SrI<sub>2</sub>(THF)<sub>5</sub>, **3**

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Compound <b>1</b>				
Sr(1)	2500	2690(1)	0	50(1)
S(1)	3684(1)	2386(2)	1410(1)	67(1)
O(1)	1676(4)	2168(3)	754(3)	72(3)
O(2)	2200(4)	3731(4)	718(4)	97(4)
C(1)	4595(5)	2072(5)	1407(4)	43(4)
Compound <b>2</b>				
Sr(1)	2500	2715(1)	0	43(1)
Se(1)	3724(1)	2604(1)	1486(1)	57(1)
O(1)	1618(3)	2206(3)	743(4)	55(3)
O(2)	2160(4)	3738(3)	686(4)	78(3)
C(1)	4666(4)	2146(4)	1480(5)	40(4)
Compound <b>3</b>				
Sr(1)	496	496	0	50(1)
I(1)	–1713(2)	2766(2)	454(1)	75(1)
O(1)	–1600	–1600	0	71(7)
O(2)	826(25)	–1257(21)	595(3)	84(9)
O(3)	2638(21)	1543(21)	398(3)	64(7)

**Table 3.** Important Bond Lengths (Å) and Angles (deg) in Sr{S(2,4,6-tBu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>(THF)<sub>4</sub>·2THF, **1**, and Sr{Se(2,4,6-tBu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>(THF)<sub>4</sub>·2THF, **2**

	Sr(SMes*) <sub>2</sub> (THF) <sub>4</sub>	Sr(SeMes*) <sub>2</sub> (THF) <sub>4</sub>
Sr–E	2.951(2)	3.066(1)
Sr–O	2.574(7)	2.590(7)
	2.565(7)	2.536(7)
E–C	1.794(9)	1.946(8)
E–Sr–E	157.1(1)	171.9(1)
E–Sr–O	80.5(1), 84.4(2)	79.7(1), 84.4(1)
	90.7(1), 114.0(2)	92.5(1), 106.9(1)
O–Sr–O	76.0(2), 77.4(3), 134.1(3), 148.2(2)	76.1(2), 76.1(3), 135.0(3), 147.5(2)
Sr–E–C	120.9(3)	117.6(2)

**Table 4.** Important Bond Lengths (Å) and Angles (deg) for SrI<sub>2</sub>(THF)<sub>5</sub>, **3**

	Sr(1)–I(1)	Sr(1)–O(2)	2.63(2)
	Sr(1)–O(1)	Sr(1)–O(3)	2.54(2)
I(1)–Sr(1)–I(1a)	178.6(1)	O(1)–Sr(1)–O(2)	70.2(4)
I(1)–Sr(1)–O(3)	87.1(4)	O(2)–Sr(1)–O(3)	71.9(6)
O(2)–Sr(1)–I(1a)	88.3(4)	O(3)–Sr(1)–O(3a)	76.2(7)
I(1)–Sr(1)–O(1)	90.7(1)	O(2)–Sr(1)–O(2a)	140.4(9)
O(3)–Sr(1)–I(1a)	91.8(4)	O(1)–Sr(1)–O(3)	141.9(4)
I(1)–Sr(1)–O(2)	92.1(4)	O(3)–Sr(1)–O(2a)	147.6(6)

50% split positions. The positions of the oxygen atom could not be located; therefore all positions were refined as carbon atoms. **3** crystallizes in the chiral space group *P*4<sub>3</sub>2<sub>1</sub>2. The correct hand of the model was determined by refining the Flack parameter,<sup>37,38</sup> which resulted in a value close to +1 and showed small standard deviation, indicating the correct handedness of the model. In **1** and **2**, all non-hydrogen atoms, except the disordered positions, were refined using anisotropic thermal parameters; in **3**, all non-hydrogen atoms were refined this way.

## Results and Discussion

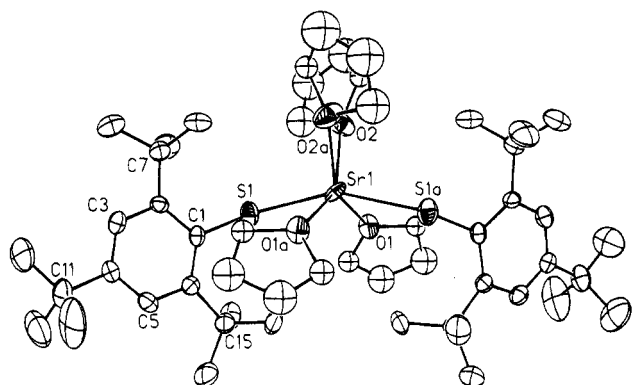
**Structural Descriptions.** Sr(SMes\*)<sub>2</sub>(THF)<sub>4</sub>·2THF **1**. The structure of **1**, shown without the THF solvent molecule present in each asymmetric unit, is pictured in Figure 1. Each asymmetric unit contains one disordered THF solvent molecule and one-half Sr(SMes\*)<sub>2</sub>(THF)<sub>4</sub> unit, the second half of which is generated by a 2-fold axis. Sr(SMes\*)<sub>2</sub>(THF)<sub>4</sub> consists of neutral, discrete, monomeric molecules with no apparent

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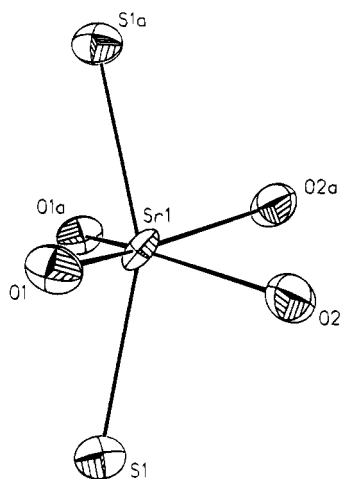
(36) Sheldrick, G. M. SHELXTL-Plus: A program package for crystal structure solution and refinement. Universität Göttingen, 1992.

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**Figure 1.** Computer-generated plot of **1** (35% ellipsoids). Hydrogen atoms have been omitted for clarity.

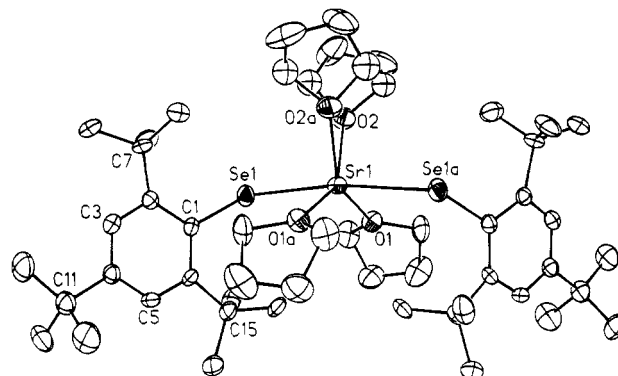


**Figure 2.** Computer-generated plot of the coordination sphere of strontium in **1**.

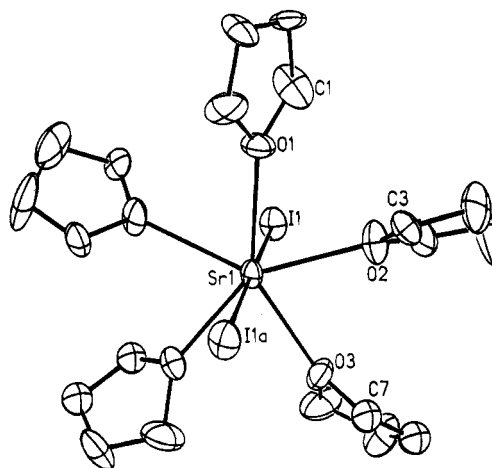
intermolecular interactions. The strontium atom displays a severely distorted octahedral geometry with two thiolato ligands and four THF molecules, the thiolato ligands in positions trans to each other. Figure 2 presents a view of the coordination sphere at Sr. The S–Sr–S angle is  $157.1(1)^\circ$ , and the angles between the THF oxygen atoms and the Sr–S axis range from  $80.5(1)$  to  $114.0(2)^\circ$ , demonstrating the high degree of distortion in this polyhedron. The angles between the four oxygen atoms are  $76.0(2)$ ,  $77.4(3)$ ,  $134.1(3)$ , and  $148.2(2)^\circ$ . The Sr–S distances are  $2.951(2)$  Å, and the Sr–O distances are  $2.565(7)$  and  $2.574(7)$  Å. The S–C bond length is  $1.794(9)$  Å, with an Sr–S–C angle of  $120.9(3)^\circ$ . The shortest Sr–H distance is  $3.152$  Å (H17a).

**Sr(SeMes\*)<sub>2</sub>(THF)<sub>4</sub>·2THF, 2.** The structure of **2** is illustrated in Figure 3 and consists of neutral discrete monomeric molecules. The structure of **2** is isomorphous with that of **1**; therefore the molecular geometries of **1** and **2** are very similar. The strontium atom is surrounded in a distorted octahedral fashion by two selenolato ligands and four THF molecules, with the selenolato ligands trans to each other. The Sr–Se distances are  $3.066(1)$  Å, and the Sr–O bond lengths are found between  $2.536(7)$  and  $2.590(7)$  Å. The Se–C distance is  $1.946(8)$  Å; the Sr–Se–C angle,  $117.6(2)^\circ$ . The Se–Sr–Se angle is almost linear, at  $171.9(1)^\circ$ . The angles between the THF oxygen atoms and the Sr–Se axis range from  $79.7(1)$  up to  $106.9(1)^\circ$ . The angles between neighboring THF oxygen atoms show a wide range of angles from  $76.1(2)^\circ$  (O(1)–Sr(1)–O(2)) up to  $147.5(2)^\circ$  (O(2)–Sr(1)–O(1a)). The shortest Sr–H interaction is  $2.946$  Å.

**SrI<sub>2</sub>(THF)<sub>5</sub>, 3.** The structure of **3**, presented in Figure 4,



**Figure 3.** Computer-generated plot of **2** (35% ellipsoids). Hydrogen atoms have been omitted for clarity.

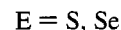
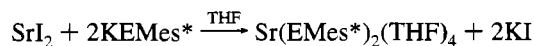


**Figure 4.** Computer-generated plot of **3** (35% ellipsoids). Hydrogen atoms have been omitted for clarity.

consists of neutral, discrete molecules. The strontium atom is located on a 2-fold axis and is surrounded in a pentagonal bipyramidal fashion by two I atoms and five THF oxygen atoms. The I–Sr–I angle is almost linear ( $178.6(1)^\circ$ ), and the five equatorial oxygen atoms form angles from  $87.1(4)$  up to  $92.1(4)^\circ$ , relative to the Sr–I axis. The angles between the THF oxygen atoms are found between  $70.2(4)$  and  $76.2(7)^\circ$ , thus representing an almost perfect pentagonal bipyramidal array. The Sr–I bond distance is  $3.230(2)$  Å; the Sr–O distances are quite diverse, at  $2.54(2)$ ,  $2.62(1)$ , and  $2.63(2)$  Å.

## Discussion

Compounds **1** and **2** were synthesized in a straightforward manner by the simple salt elimination reaction between SrI<sub>2</sub> and 2 equivalents of the respective potassium thiolate or selenolate in THF:



Attempts to prepare **1** and **2** by the reaction of Li(THF)<sub>3</sub>SMes\* or Li(THF)<sub>3</sub>SeMes\* with SrI<sub>2</sub>(THF)<sub>5</sub>, even under refluxing conditions, resulted only in the recovery of the starting materials. The driving force for the above reactions seems to be the formation of KI. Apparently, the lattice energy of LiI is not high enough to allow the desired reactions to proceed. Also, the reactivities of LiEMes\* are lower than those of KEMes\*, due to a reduced polarization of the metal–chalcogen bond.

**1** and **2** are oxygen- and moisture-sensitive colorless compounds, which are quite stable if stored under inert gas

atmosphere. The use of the sterically demanding ligand system  $-E-2,4,6-tBu_3C_6H_2$  ( $E = S, Se$ ) allows the isolation of discrete monomeric molecules. The effectiveness of these ligands in stabilizing low-coordinate or monomeric compounds has been shown previously with the isolation of a variety of group 12, group 13, and transition metal thiolates and selenolates, exhibiting low coordination numbers.<sup>39-41</sup>  $SrI_2(THF)_5$ , **3**, the apparent starting material for the above reactions, can be isolated in good yield by dissolving  $SrI_2$  in THF. If the mother liquor is removed, **3** is unstable, even under inert gas atmosphere, presumably due to the loss of THF.

**1** and **2** are isomorphous and show very similar structural motifs. The central Sr atom is surrounded in a considerably distorted octahedral fashion by two sterically encumbered organochalcogeno groups, located in trans positions relative to each other, and four THF oxygen atoms. The major difference between the compounds lies in the degree of distortion apparent in the polyhedron as exemplified by the angle between the two organochalcogeno ligands and the central Sr atom. The S—Sr—S angle is  $157.1(1)^\circ$  for **1** (see also Figure 2) and  $171.9(1)^\circ$  for the corresponding selenolate **2**. The addition of covalent radii of S and Se (1.02 and 1.17 Å)<sup>42</sup> and the metallic radius for Sr (2.15 Å)<sup>43</sup> results in a calculated Sr—S distance of 3.17 Å and a Sr—Se bond length of 3.32 Å. If these values are corrected for ionic contribution using the Schomaker—Stevenson formula,<sup>44</sup> slightly shorter values (3.038 Å (Sr—S) and 3.184 Å (Sr—Se)) are obtained. A comparison of these values with experimental data derived from the crystal structure analyses shows significant differences (Sr—S<sub>obs</sub> 2.951(2) Å, Sr—Se<sub>obs</sub> 3.066(1) Å), which might be accredited to the large metallic radius of Sr that was derived from the bulk metal in which Sr displays a coordination number of 12. The comparison of the Sr—S bond length of **1** with that of  $SrS_2C_4N_2 \cdot 5H_2O$ <sup>45</sup> shows very similar values (2.951(2) vs 2.974(4) Å). The slightly longer Sr—S bond length in  $SrS_2C_4N_2 \cdot 5H_2O$  can be explained by the increased coordination number (7 + 2 vs 6 in **1**).<sup>45</sup> A comparison of the Sr—Se bond length of **2** with that of  $Sr\{SeSi(SiMe_3)_3\}_2(TMEDA)_2$ <sup>32</sup> shows significantly different values, 3.066(1) Å for **2** vs 2.946(1) Å for  $Sr\{SeSi(SiMe_3)_3\}_2(TMEDA)_2$ . The large difference in bond length observed in the two compounds displaying identical coordination numbers might be explained by the difference in steric bulk apparent in the  $-Si(SiMe_3)_3$  and the 2,4,6-*t*Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub> ligand, with the Mes\* group causing larger steric repulsion, resulting in bond elongation. The shortest Sr—H distance observed in **1** is 3.152 Å (H17a), located at the ortho *t*Bu group of the Mes\* ligand. This interaction is well in the range of van der Waals interactions but cannot be described as significant. The shortest Sr—H interaction in **2** is 2.946 Å; no apparent distortions in the ortho *tert*-butyl group are observed. The large Sr—E—C angles in **1** ( $120.9(1)^\circ$ ) and **2** ( $117.6(2)^\circ$ ) ( $E = S, Se$ ) reflect the wide array of possible M—E—C angles reported so far. There is no apparent correlation between bond characteristics or degree of bulk in the ligand and metal—E—C angle or the interaction of ortho substituents at the ligands with the metal center. This is

demonstrated by in the monomeric iron thiolate  $Fe\{S(Mes_2C_6H_3)\}_2$ , with Fe—S—C angles of  $106.2(2)$  and  $108.7(3)^\circ$ ,<sup>46</sup> the cadmium thiolate  $(NEt_4)_2[Cd(S-o-SiMe_3C_6H_4)_4]$ , with a Cd—S—C angle of  $115.5(9)^\circ$ ,<sup>47</sup> the monomeric zinc selenolate  $Zn\{Se(2,6Mes_2C_6H_3)\}_2$ , displaying a Zn—Se—C angle of  $102.2(2)^\circ$ ,<sup>41</sup> the gallium tris(selenolate)  $Ga(SeMes^*)_3$ , with an average Ga—Se—C angle of  $93.9^\circ$ ,<sup>48</sup> or the magnesium thiolate and selenolate  $Mg(EMes^*)_2(L)_2$ , with M—S—C angles of  $116.6(1)$  and  $117.1(1)^\circ$  and Mg—Se—C angles of  $100.7(2)$  and  $101.8(2)^\circ$ .<sup>9</sup>

A comparison of structural features of thiolato and selenolato derivatives known for alkaline-earth elements clearly shows a relationship between coordination number and ionic radius: the Be species  $Be(SMes^*)_2(OEt_2)_8$  exhibits a distorted three-coordinate metal center, whereas  $Mg(SMes^*)_2(THF)_2$  is observed as a distorted four-coordinate bis(etherate).<sup>9</sup> The strontium derivative presented here displays a distorted six-coordinate environment at the metal center, with the selenolato derivatives showing an identical trend. This increase of coordination number follows smoothly the increase of ionic radii.

$SrI_2(THF)_5$ , **3**, exhibits pentagonal bipyramidal geometry, which agrees with the observation that heavy alkaline-earth derivatives often show unusual coordination geometries.<sup>3</sup> The three possible arrangements described for coordination number 7 are the pentagonal bipyramid (1:5:1 structure), the capped octahedron (1:3:3 structure), and the capped trigonal prism (1:4:2 structure).<sup>42</sup> Theoretical calculations have shown that the capped octahedron is the energetically most favored.<sup>49</sup> However, the interconversion between the three modifications requires only very little energy. Therefore, many examples with intermediate geometries are known, whereas only few compounds with perfect capped octahedral, capped trigonal prismatic, or pentagonal bipyramidal geometry have been reported.<sup>42</sup> Examples of species displaying pentagonal bipyramidal geometry include  $IF_7$ ,<sup>42</sup>  $TeF_7^-$ ,<sup>50</sup>  $CH_3OTeF_6^-$ ,<sup>50</sup>  $ZrF_7^{3-}$ ,<sup>51</sup>  $Mn(BF_4)_2$ ,<sup>52</sup>  $NdCl_3 \cdot 4THF$ ,<sup>53</sup> and the samarium cation  $SmI_2(THF)_5^+$ .<sup>54</sup> An example of a related six-coordinate alkaline-earth etherate was published recently.<sup>55</sup>  $CaI_2(THF)_4$  displays octahedral geometry with the two I anions trans to each other. The higher coordination number observed in **3** in comparison to  $CaI_2(THF)_4$  is caused by the increased ionic radius of Sr in contrast to Ca, an identical trend observed for alkaline-earth organochalcogenides, as described above.

## Conclusions

We synthesized and characterized two examples of strontium bis(thiolates) and -(selenolates). The use of the sterically demanding ligand  $-E(2,4,6-tBu_3C_6H_2)$  ( $E = S, Se$ ) allowed the isolation of neutral, monomeric tetraetherates displaying dis-

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torted octahedral geometry at the Sr center. We also reported the structural characterization of  $\text{SrI}_2(\text{THF})_5$ , displaying almost perfect pentagonal bipyramidal geometry at the strontium atom. Work in this area of research is continuing.

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**Supplementary Material Available:** Full tables of data collection parameters, atom coordinates, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters (24 pages). Ordering information is given on any current masthead page.

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