

Barium Thiolates and Selenolates: Syntheses and Structural Principles

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Dedicated to Professor Ulrich Müller on the occasion of his 60th birthday

Abstract: The synthesis and structural characterization of a family of barium thiolates and selenolates is described. The thiolates were synthesized by metalation of thiols, the selenolates by reductive insertion of the metal into the selenium–selenium bond of diorganodiselenides. Both reaction sequences were carried out by using barium metal dissolved in ammonia; this afforded barium thiolates and selenolates in good yield and purity. The structural principles displayed in the target compounds span a wide range of solid-state formu-

lations, including monomeric and dimeric species, and separated ion triples, namely [Ba(thf)₄(SMes*)₂] (**1**; Mes* = 2,4,6-tBu₃C₆H₂), [Ba(thf)₄(SeMes*)₂] (**2**), [Ba([18]crown-6)(hmpa)₂][(SeMes*)₂] (**3**), the dimeric [[Ba(py)₃(thf)(SeTrip)₂]₂] (**4**; py = pyridine, Trip = 2,4,6-*i*-Pr₃C₆H₂), and [Ba([18]crown-6)(SeTrip)₂] (**5**). The full range of association modes is com-

pleted by [Ba([18]crown-6)(hmpa)S-Mes*][SMes*] (**6**) communicated earlier by this group. In the solid state, this compound displays an intermediate ion coordination mode: one anion is bound to the metal, while the second one is unassociated. Together these compounds provide structural information about all three different association modes for alkaline earth metal derivatives. This collection of structural data allows important conclusions about the influence of solvation and ligation on structural trends.

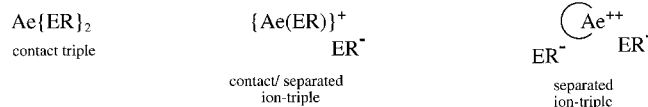
Keywords: barium · chalcogens · coordination chemistry · structure elucidation · synthesis design

Introduction

Chalcogenolate derivatives of the heavy alkaline earth metal barium have been well established for oxygen-based compounds owing to their potential as precursor materials for high temperature superconductors.^[1] In contrast, much less attention has been devoted towards the heavier chalcogen congeners,^[2] despite their potential in the production of phosphor materials and two-color IR windows.^[3] Structurally authenticated examples are limited to the sulfur derivatives [[Ba(H₂O)₄(tmtH₂)₂]_{*n*}] (tmt = 2,4,6-trimercaptotriazine, S₃C₃N₃),^[4] [Ba([18]crown-6)(hmpa)SMes*][SMes*] (hmpa = hexamethylphosphoramide; Mes* = 2,4,6-tBu₃C₆H₂),^[5] [Ba(hmpa)₃-{NaphNNNC(S)}₂],^[6] [Ba(hmpa)₃(C(=S)NOPh)₂],^[7] and the tellurolate [Ba(py)₅(TeSi(SiMe₃)₂)₂] (py = pyridine).^[8] A few more compounds have been reported, including [Ba(SCMe₃)₂],^[9] [Ba(tmeda)₂(SeSi(SiMe₃)₂)₂],^[8] and [Ba(thf)₄(TeSi(SiMe₃)₂)₂],^[8] but structural data are not available.

As indicated by this short list of compounds, little is known about barium thiolates and tellurolates, but information is even more scarce for the selenolates; only [Ba(tmeda)₂-

(SeSi(SiMe₃)₂)₂] is mentioned.^[8] As a consequence, few data are available with regard to synthetic strategies or the structure-determining influence of ligation, donation, and solvation. This information is crucial if the compounds are to be used in the production of solid-state materials, since the structural features of a precursor are closely linked to the physical condition necessary for its transformation into the desired solid-state material. This argument is especially significant for alkaline earth metal derivatives, since three different types of ionic association may be observed: contact triples, with two cation–anion linkages, separated ions, with isolated cations and anions, and an intermediate, with one cation–anion linkage and one unassociated anion (Scheme 1).



Scheme 1. The three different ion association modes in alkaline earth metal derivatives.

Only recently, the first structural characterization of an alkaline earth metal derivative with an intermediate ion association was published by this group,^[5] and information on how the structural features of the target compounds may be affected remains scarce. Since the mode of association has a

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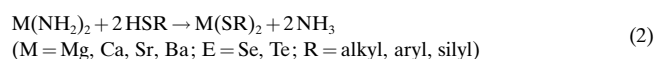
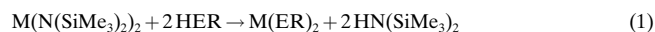
severe effect on the physical properties of the target compounds, it is necessary to evaluate structure-determining factors before the compounds may be used as precursor materials. Moreover, the type of ion association observed in either solution or solid state will provide important information about metal–ligand and metal–donor bond strengths and characteristics.

Since little is known about alkaline earth metal chalcogenolates, information about metal–ligand bond characteristics is scarce. Experimental and theoretical studies reported heavy alkaline earth metal derivatives to deviate from idealized geometry.^[10] Well-documented examples include cyclopentadienyl and halide derivatives, with ligand–metal–ligand angles decreasing to about 150° for the heavier, two-coordinate (gas-phase) species. The comparison of geometrical features in [Ba(thf)₄(SMes*)₂] (**1**; Mes* = 2,4,6-tBu₃C₆H₂), and [Ba(thf)₄(SeMes*)₂] (**2**) with their calcium and strontium analogues will reveal if related structural trends are observed for the chalcogenolates. This study will yield important information about bonding characteristics in this scarcely studied group of compounds.

We here present a family of barium thiolates and selenolates, [Ba(thf)₄(SMes*)₂] (**1**), [Ba(thf)₄(SeMes*)₂] (**2**), [Ba([18]crown-6)(hmpa)₂][(SeMes*)₂] (**3**), [[Ba(py)₃(thf)(SeTrip)₂]₂] (**4**; Trip = 2,4,6-*i*Pr₃C₆H₂), and [Ba([18]crown-6)(SeTrip)₂] (**5**), which provide the first structural data for barium selenolates and additional information to the only scarcely explored family of thiolates. By including the previously communicated [Ba([18]crown-6)(hmpa)SMes*]-[SMes*] (**6**) in the discussion,^[5] we are able to compare all possible modes of ion association. We also present information on synthetic accessibility, and the influence of ligands and donors on the structural features of this group of compounds.

Results

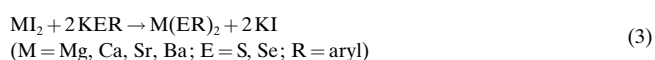
Several routes towards the target compounds can be envisioned, including transamination, salt elimination, and metallation. Arnold et al. utilized transmetallation involving bis-(bistrimethylsilyl)amides for the synthesis of strontium and barium selenolates and tellurolates [Eq. (1)].^[8, 11] Purdy et al. synthesized calcium, strontium and barium thiolates using the same principle, but relying on M(NH₂)₂ [Eq. (2)].^[9]



Typically, the target compounds are obtained in good yield and purity, and a wide variety of solvents, ligands, and donors may be employed. However, use of small highly acidic chalcogenols in conjunction with bis-(bistrimethylsilyl)amides induces a yield-reducing side reaction.^[12] The protonation of the liberated secondary amine with unreacted chalcogenol under formation of the chalcogeno ether and primary amine is

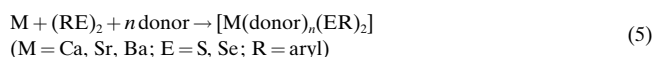
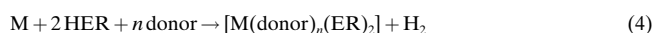
observed. A second protonation transforms the primary amine into ammonia; a third protonation step results in the formation of an ammonium salt. Accordingly, transamination is limited to either the less acidic aliphatic or sterically demanding aromatic chalcogenols. Transamination also requires the synthesis of alkaline earth metal amides, and a supply of highly oxygen-sensitive selenol, available by reduction of diorganodiselenides. The reduction typically occurs in 60% yield;^[13] this results in significant loss of starting material.

A salt-elimination regime has been used successfully for the synthesis of [Sr(thf)₄(EMes*)₂] (E = S, Se).^[14] Importantly, the reaction required the combined use of strontium iodide and potassium thiolate or selenolate, owing to the limited solubility of strontium chloride and bromide and the high solubility of lithium and sodium iodides in ether-type solvents [Eq. (3)].



This route also requires the reduction of diorganodiselenide to selenol (vide supra).^[14] The subsequent reaction of the chalcogenol with potassium hydride in the presence of donor yields the alkali metal salts in good yield and purity.^[15] The solubility of the alkaline earth metal iodides remains limited, and use of THF as a solvent is required.

Metallation has been used successfully for the synthesis of calcium,^[16] strontium,^[5] and barium thiolates and selenolates, including the compounds presented in this manuscript. Two variations of this scheme are possible: the reaction of alkaline earth metal with two equivalents of chalcogenol [Eq. (4)] or the reaction of diorganodichalcogenide with alkaline earth metal [Eq. (5)].



The reactions were carried out in dry liquid ammonia, in order to ensure the formation of highly reactive metal centers. Calcium, strontium, and barium easily dissolve in ammonia, whereas magnesium requires the use of finely dispersed powder. A significant increase in reactivity is observed on descending the group of alkaline earth metals. The reaction of calcium with thiol or diorganodiselenide requires extended reflux times (6–12 hours) in liquid ammonia,^[16] whereas the heavier metals react within 1–2 hours.^[5]

The synthetic variations shown in Equations (4) and (5) may be utilized for the synthesis of all chalcogenolates. However, Equation (4) is most advantageous for the preparation of thiols, since thiols can generally be synthesized directly and be stored indefinitely without oxidation. The corresponding selenols rapidly oxidize to diorganodiselenides; therefore, reduction is required, which reduces the yield. Reductive insertion, as described in Equation (5), avoids the use of selenol, rather the stable diorganodiselenide can be employed.

Two different sterically encumbered organic groups were utilized to ensure the isolation of soluble, nonpolymeric products: Mes* (Mes* = 2,4,6-tBu₃C₆H₂) and Trip (Trip = 2,4,6-*i*Pr₃C₆H₂). The reactions were carried out in THF under addition of anhydrous liquid ammonia, in order to increase the reactivity of the metal and ensure a homogenous reaction. Donors such as [18]crown-6, hmpa, and pyridine were included in the reaction mixture. The reactions afforded the target compounds in good yield and purity. All compounds are colorless or pale yellow species that are oxygen and moisture sensitive, but are quite stable if stored under inert gas. Upon exposure to air, the selenolates quickly turn orange to deep red, indicating the formation of diorganodiselenides.

Structural descriptions: Crystallographic information for compounds **1–5** is summarized in Table 1 and in the Experimental Section. A compilation of pertinent bond lengths and angles for all compounds is given in Table 2, while Figures 1–6 illustrate the structural principles displayed in compounds **1–6**. In most complexes, geometrical data for the respective donor and chalcogenolate anion were unexceptional and can be found in greater detail in the deposited crystal structure data.

[Ba(thf)₄(SMes*)₂] (1): Compound **1** (which is isomorphous with compound **2**, see below) consists of neutral, discrete, monomeric molecules with six-coordinate, pseudo-octahedral barium centers. The two thiolate ligands are oriented approx-

Table 1. Crystallographic data for compounds **1–5**.

	1	2	3	4	5
formula	C ₆₀ H ₁₀₆ BaO ₆ S ₂	C ₆₀ H ₁₀₆ BaO ₆ Se ₂	C ₆₀ H ₁₁₈ BaN ₆ O ₈ P ₂ Se ₂	C ₄₉ H ₆₉ BaN ₃ OSe ₂	C ₃₀ H ₃₆ BaO ₈ Se ₂
<i>M_w</i>	1124.91	1218.71	1408.80	1011.33	1110.45
<i>a</i> [Å]	18.3140(6)	18.5289(6)	10.6373(1)	13.5589(1)	11.527(2)
<i>b</i> [Å]	19.3695(6)	19.3261(6)	17.3387(1)	13.6038(2)	27.613(3)
<i>c</i> [Å]	18.6726(6)	18.5810(5)	19.9426(1)	15.0013(1)	17.613(3)
α [°]				82.369(1)	
β [°]	107.709(1)	108.100(2)	91.707(1)	71.655(1)	103.01(1)
γ [°]				72.746(1)	
<i>V</i> [Å ³]	6309.9(3)	6324.4(3)	3676.52(4)	2505.84(4)	5462(1)
<i>Z</i>	4	4	2	2	4
space group	<i>I</i> 2/ <i>a</i>	<i>I</i> 2/ <i>a</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
ρ_{calc} [g cm ⁻³]	1.184	1.280	1.273	1.340	1.350
μ [mm ⁻¹]	0.739	1.823	1.623	2.280	2.106
<i>T</i> [K]	150	125	120	150	150
2 θ range [°]	3.1–50.0	3.1–50.0	3.1–56.6	2.86–56.54	2.8–56.7
independent reflns	5495	5570	8740	11542	13033
observed reflns [<i>I</i> > 2 σ (<i>I</i>)]	3741		7801	10331	9613
parameters	280	321	359	512	540
<i>R</i> 1 (all data)	0.0881	0.1072	0.0275	0.0342	0.0918
<i>wR</i> 2 (all data)	0.1392	0.2018	0.0544	0.0714	0.1236
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0561	0.0677	0.0225	0.0289	0.0596
<i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.1273	0.1759	0.0526	0.0686	0.1129

Table 2. Selected bond lengths [Å] and angles [°] for barium thiolates, selenolates, and tellurolates.

	Ba–E	Ba–donor	E–Ba–E	Ba–E–C	CN ^[a]	Ref.
[Ba(thf) ₄ (SMes*) ₂] (1)	3.133(2)	2.731(7)–2.737(3)	155.17(5)	111.7(1)	6	[b]
[Ba(hmpa) ₃ (C(=S)NPh) ₂]	3.31(1)	N: 2.91(2) ^[c] hmpa: 2.60(3)	–	–	7	[7]
[Ba(hmpa) ₃ {NaphNNNN(C(S)) ₂ }]	3.31(1)	N: 2.86(1) ^[c] hmpa: 2.59(1)	–	–	7	[6]
[Ba(18C6)(hmpa)(SMes*)][SMes*] (6)	3.012(2) 3.025(2)	18C6: 2.772(5)–2.807(5) hmpa: 2.593(5)	172.8(1) 174.1(1) ^[d]	150.8(2) 153.7(3)	8	[5]
[Ba(H ₂ O) ₄ (H ₂ ,4,6-S ₃ C ₃ N ₃) ₂]	3.396(2)–3.629(2)	N: 2.99–3.05 ^[c] H ₂ O: 2.804(5)–2.983(5)	–	–	10	[4]
[Ba(thf) ₄ (SeMes*) ₂] (2)	3.279(1)	2.732(7)–2.738(4)	158.65(4)	106.3(2)	6	[b]
[{Ba(py) ₃ (thf)(SeTrip) ₂ }] ₂ (4)	3.2973(3) ^[e] 3.4189(3) ^[e] 3.2768(3) ^[f]	py: 2.825(2)–2.910(2) thf: 2.823(2)	129.14(1) 60.40(1) 146.51(1) $\Sigma = 336.05$	111.82(6) 122.42(7)	7	[b]
[Ba(18C6)(hmpa) ₂][(SeMes*) ₂] (3)	–	18C6: 2.780(1)–2.791(1) hmpa: 2.587(1)	–	–	8	[b]
[Ba(18C6)(SeTrip) ₂] (5)	3.2326(7) 3.2361(7)	2.767(3)–2.803(3)	155.00(2)	93.3(1) 96.1(1)	8	[b]
[Ba(py) ₃ {TeSi(SiMe ₃) ₃ }] ₂	3.382(1)	2.856(4)–2.934(5)	171.91(2)	144.42(3) ^[g]	7	[8]

[a] CN = coordination number of barium. [b] This work. [c] Intramolecular interaction. [d] O(hmpa)-Ba-S angle. [e] Bridging. [f] Terminal. [g] Ba-Te-Si angle.

imately *trans* to each other, as evidenced by the S–Ba–S angle of $155.17(5)^\circ$. The distorted octahedral geometry is also evidenced by the angles between the THF oxygen atoms and the Ba–S axis ranging from $76.74(7)^\circ$ to $115.0(4)^\circ$. The angles between the four oxygen atoms are $73.9(5)^\circ$, $77.2(2)^\circ$, $137.4(2)^\circ$, and $147.7(6)^\circ$; again this emphasizes the severe distortion around barium. The Ba–S bond length is $3.133(2) \text{ \AA}$, Ba–O contacts are observed at $2.731(7)$ and $2.737(3) \text{ \AA}$. The S–C bond length is $1.771(4) \text{ \AA}$, with a Ba–S–C angle of $111.7(1)^\circ$.

[Ba(thf)₄(SeMes*)₂] (2): The structure of compound **2**, presented in Figure 1, is isomorphous with compound **1**. The Se–Ba–Se angle is observed at $158.65(4)^\circ$; the angles between

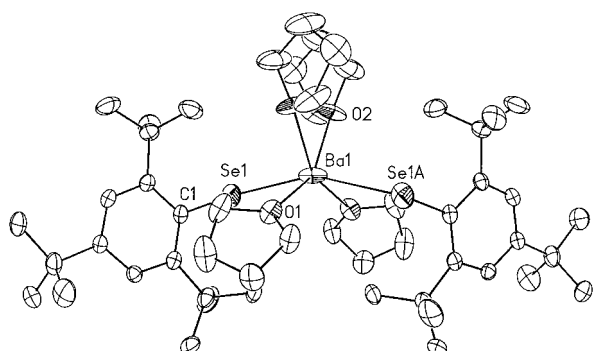


Figure 1. Crystal structure of **2** with anisotropic displacement parameters depicting 30% probability. The hydrogen atoms have been omitted for clarity.

the thf oxygens and the Ba–S axis range from $77.12(9)^\circ$ up to $114.4(12)^\circ$. The angles between the thf oxygen atoms are observed between $69.1(8)^\circ$ to $155.0(9)^\circ$. The Ba–Se bond length is $3.2787(11) \text{ \AA}$, and the Ba–O bond lengths are $2.732(7)$ – $2.738(4) \text{ \AA}$. The Se–C bond lengths is $1.930(6) \text{ \AA}$, with a Ba–Se–C angle of $106.3(2)^\circ$.

[Ba([18]crown-6)(hmpa)₂][(SeMes*)₂] (3): The crystal structure of **3** reveals a completely separated ion triple with a formal separation of cation and anions of more than 6 \AA . Figure 2 presents a view of the cation, in which an [18]crown-6

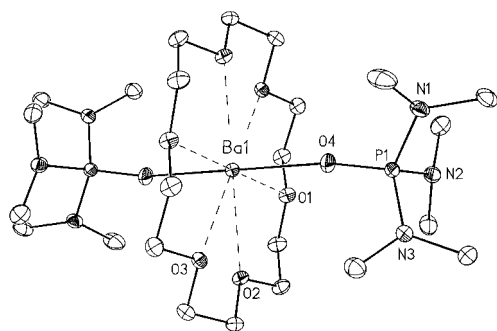


Figure 2. Crystal structure of **3** with anisotropic displacement parameters depicting 30% probability. Only the cation is shown; hydrogen atoms have been omitted for clarity.

and two hmpa molecules are coordinated to the barium center. Figure 3 shows cation and anions. Barium is located on a center of symmetry; accordingly, one half of the crown ether, one hmpa molecule, and one selenolate anion are contained in the asymmetric unit. Barium is eight coordinate,

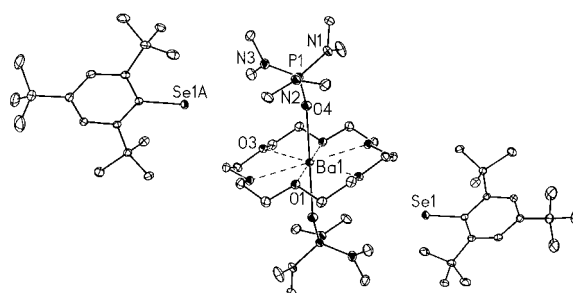


Figure 3. Crystal structure of **3** with anisotropic displacement parameters depicting 30% probability. The hydrogen atoms have been omitted for clarity.

with Ba–O crown ether bond lengths ranging from $2.780(1)$ – $2.791(1) \text{ \AA}$, and hmpa Ba–O contacts of $2.587(1) \text{ \AA}$. The selenolate anions display Se–C bond lengths of $1.9243(14) \text{ \AA}$.

[(Ba(py)₃(thf)(SeTrip)₂)]₂ (4): The structure of **4** is presented in Figure 4. The compound crystallizes as a dimer. The two halves of the molecule are related by a center of symmetry located in the center of the Ba₂Se₂ ring; this results in planar

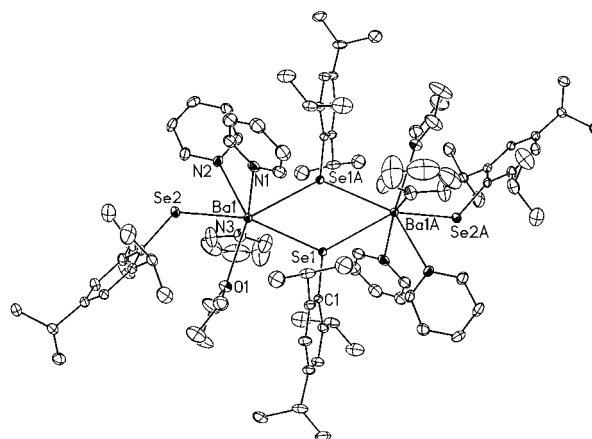


Figure 4. Crystal structure of **4** with anisotropic displacement parameters depicting 30% probability. The hydrogen atoms have been omitted for clarity.

ring geometry. Each barium is connected to two selenolate ligands, one bridging, the other terminal. In addition, there are three pyridine donors and one thf donor, which leads to a coordination number of seven for barium. The bridging between the two barium centers is asymmetric with a short Ba–Se bond length of $3.2973(3) \text{ \AA}$ and a longer one of $3.4189(3) \text{ \AA}$. The terminal Ba–Se bond length is observed at $3.2768(3) \text{ \AA}$. There is an acute angle within the four membered ring at barium of $60.40(1)^\circ$, while the angle at the bridging selenium is obtuse with $119.599(7)^\circ$.

[Ba[18]crown-6)(SeTrip)₂] (5): Compound **5**, depicted in Figure 5, displays an eight-coordinate barium center surrounded by an [18]crown-6 molecule in addition to two selenolate ligands, arranged approximate *trans* to each other

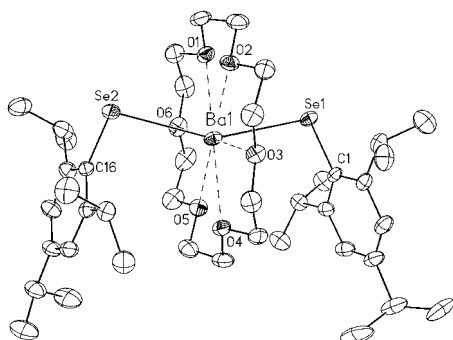


Figure 5. Crystal structure of **5** with anisotropic displacement parameters depicting 30% probability. The hydrogen atoms have been omitted for clarity.

(Se–Ba–Se 155.00(2)°). The Ba–O (crown ether) bond lengths range between 2.767(3) and 2.803(3) Å. The Ba–Se bond lengths are very similar with 3.2326(7) and 3.2361(7) Å. The Ba–Se–C angles are narrow with 93.3(1)° and 96.1(1)°.

Discussion

Synthetic access to alkaline earth metal chalcogenolates is possible by a variety of methodologies, which include transamination, salt elimination, and metallation. Low solubility or inaccessibility of certain starting materials preclude the utilization of other strategies. For example, alkane elimination, applied extensively in the synthesis of magnesium chalcogenolates^[2, 17] is not applicable, since the organometallic starting materials are not readily available. For the synthesis of heavy alkaline earth metal derivatives, metallation is preferred owing to the ease of the reaction and the cleanliness of the reaction products. Importantly, no extensive precursor preparations are necessary.

Compounds **1–5** were synthesized by metallation. Two variations of this reaction [Eqs. (4) and (5)], depending on the chalcogen substrate, were utilized. Thiolates are most conveniently synthesized by the reaction of the alkaline earth metal with two equivalents of thiol [Eq. (4)], whereas selenolates were prepared by reductive insertion [Eq. (5)] of the metal into the selenium–selenium bond of diorganodiselenide. Disadvantages of the metallation route involve limitations with respect to potential ligand systems. Exposure of the highly acidic arylthiols HSC₆H₅ or HSC₆F₅ to liquid ammonia results in acid–base chemistry and consequent deprotonation of the thiol under formation of ammonium salts; this is illustrated by the isolation of the two-dimensional network polymer [(NH₄)(py)(SC₆F₅)_n]_n.^[16]

Only little information is available with regards to barium thiolates, selenolates, and tellurolates. This paper presents the first structural characterization of barium selenolates, in addition to data that completes the array of alkaline earth

ion-association modes: compounds **1**, **2**, **4**, and **5** display contacts between cation and anions, compound **3** exhibits separated cation and anions, and **6** (Figure 6) represents an intermediate.

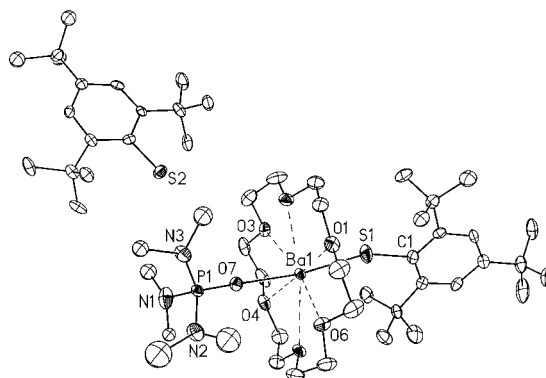


Figure 6. Crystal structure of **6** with anisotropic displacement parameters depicting 30% probability. The hydrogen atoms have been omitted for clarity.

Coordination numbers in known barium thiolates range from six to ten. Accordingly, a range of barium–sulfur bond lengths from 3.133(2) Å for the six coordinate **1**, to 3.629(2) Å for the ten coordinate [Ba(H₂O)₄(tmtH₂)₂]_n is observed.^[4] Other barium–sulfur bond lengths fall in this range, with the exception of the eight coordinate compound **6** with Ba–S bond lengths of 3.012(2) and 3.025(2) Å; these short bonds can be attributed to the cationic nature of the complex.^[5] The observed bond lengths agree well with the sum of ionic radii, with 3.19 Å for six coordinate Ba²⁺ and S²⁻ or 3.26 Å for eight coordinate Ba²⁺ and six coordinate S²⁻.^[18] The slightly shorter experimental values may be explained by the coordination number of six listed for S²⁻.

Barium selenolates display very comparable trends, and coordination numbers range from six to eight. The six coordinate **2** displays Ba–Se bond lengths of 3.279(1) Å; a slightly shorter value than the sum of ionic radii for six-coordinate Ba²⁺ and Se²⁻ (3.33 Å).^[18] Barium–selenium bond lengths for the seven coordinate dimeric **4** are observed at 3.2768(3) (terminal), 3.2973(3) (bridging) and 3.4189(3) Å (bridging). The two significantly different bridging distances within the four-membered Ba₂S₂ ring imply a weak bridging interaction. Compound **4** represents a rare example of higher aggregation in this group of compounds; most known derivatives are monomeric. The weak bridging interaction observed in **4** provides a possible explanation for the rare occurrence of higher oligomers. This point is further strengthened by the difficulties encountered to reproduce the synthesis of compound **4**. Typically, product mixtures involving different degrees of solvation are obtained. NMR experiments suggest the existence of monomeric species in solution, supporting the view that the dimeric species is only loosely connected, and a monomer is easily obtained by solvation.

The barium–selenium bond length in the eight coordinate **5** demonstrates that bond lengths and coordination number arguments need to be carefully considered. The Ba–Se bond lengths in the eight coordinate **5** (3.2326(7), 3.2361(7) Å) are

slightly shorter than those observed for the six coordinate **2** (3.279(1) Å). Comparison of the geometry of the crown ether located in the equatorial plane of **5** with the four equatorial thf donors in **2** indicates that both sets of donors occupy about the same amount of space, effectively reducing the impact of the increased coordination number. The smaller steric requirement of the Trip as relative to that of the Mes* ligand also contributes to the shorter Ba–Se bond. A similar trend has been observed in magnesium thiolates, in which the Mg–S bond length of the seven coordinate [Mg([15]crown-5)(SCPPh₃)₂] is almost identical with related six-coordinate species.^[17b, 19]

Compounds **1** and **2** are isomorphous, with an approximate octahedral geometry about barium. The analysis of structural parameters observed in closely related calcium,^[20] strontium,^[14] and barium thiolates and selenolates of the formula [M(thf)₄(EMes*)₂], (E = S, Se) (Table 3) indicates a trend

Table 3. Comparison of bond lengths [Å] and angles [°] in [M(thf)₄(EMes*)₂].

	M–E	E–M–E	Ref.
[Ca(thf) ₄ (SMes*) ₂]	2.8177(8)	171.56(5)	20
[Ca(thf) ₄ (SeMes*) ₂]	2.9336(4)	175.40(5)	20
[Sr(thf) ₄ (SMes*) ₂]	2.951(2)	157.1(1)	14
[Sr(thf) ₄ (SeMes*) ₂]	3.066(1)	171.9(1)	14
[Ba(thf) ₄ (SMes*) ₂]	3.133(2)	155.17(5)	[a]
[Ba(thf) ₄ (SeMes*) ₂]	3.279(1)	158.65(4)	[a]

[a] This work.

with ligand-metal-ligand angles decreasing from almost linear geometry for the calcium compounds (171.56(5)° for the thiolate, and 175.40(5)° for the selenolate) to quite severe bending for the barium derivatives (155.17(5)° for **1**, and 158.65(4)° for **2**).

The comparison of bending characteristics involving the thiolates and selenolates shows the distortion to be more severe for the thiolates. This is a puzzling observation, considering that the resulting donor–ligand repulsion would be more severe for the thiolates, due to the shorter metal–ligand bond lengths (in average 0.15 Å). This unexpected result indicates that steric arguments cannot be used to explain the observed structural trends. Two alternative arguments can be employed to rationalize the distortion: if one assumes predominately ionic bonding between the metal and the ligands, which is supported by the facile formation of compounds **3** and **6**, the interaction between metal and ligands will be mainly electrostatic. As a result, packing effects might contribute significantly towards the observed distortion from ideal octahedral geometry. The deviation from octahedral geometry in [M(thf)₄(EMes*)₂] (M = Ca, Sr, Ba, E = S, Se) may also be compared with other alkaline earth metal derivatives.^[10] Crystallographic data for bis(cyclopentadienyl) derivatives, or certain dihalides of magnesium, calcium, strontium, and barium indicate an increased degree of bending upon descending the group. Theoretical calculations^[10i] verified the suggestion by Hayes^[10i] that these distortions might be due to d-orbital participation in the small, but significant degree of covalent bonding. The heavier

cations are also more easily polarized by the ligands and their larger radii render repulsion effects less severe. Supporting this line of argumentation, the Se–Ba–Se angle in **5** is almost identical with that in **2**, illustrating that changes in donor composition and ligand bulk do not direct the distortion, rather crystal packing effects, d-orbital involvement and polarization effects seem to determine the structure.

As a result of the strong solvation provided by the [18]-crown-6 macrocycle and hmpa, separation of cation and anions may be affected. The combined use of crown ether and hmpa affords a very favorable cation coordination, as observed previously for the strontium thiolate [Sr([18]-crown-6)(hmpa)₂][(SMes*)₂].^[5] Compound **3** displays separated cation and anions, whereas compound **6** has a barium center connected to one thiolate, while the second anion is separated. Both compounds were synthesized by addition of crown ether and excess hmpa, but different products were isolated.

Steric arguments can be made to explain the formation of compounds **3** and **6**. Crown ether provides effective steric saturation in the equatorial plane. Steric saturation in the axial positions depends heavily on the cation size. For example, a thf-saturated intermediate, [Ca([18]crown-6)(thf)(SeMes*)][SeMes*] has been identified for calcium,^[20] whereas the larger strontium required the addition of hmpa to induce ion separation, as demonstrated by the isolation of [Sr([18]-crown-6)(hmpa)₂][(SMes*)₂]^[5] and [Sr([18]-crown-6)(hmpa)₂][(SeMes*)₂].^[21] The larger barium center may accommodate a sterically more demanding ligand under formation of a metal–ligand bond. Compound **6** displays one barium–sulfur interaction; the second axial site is occupied by hmpa. As a result of the effective larger steric demand of the SMes* ligand and the resulting ligand–donor repulsion, the crown ether is distorted towards the hmpa. The smaller strontium cation with its shorter metal–ligand bond cannot accommodate a crown ether and EMes* ligand. The significant donor–ligand repulsion, and the resulting bond weakening, will favor the formation of donor-saturated separated species. Based on steric arguments the formation of a barium–selenium bond should be possible. However, the competition between ligation and donation, involving the strong donor hmpa and the weakly bonding selenolate ligand, shows ligation to be energetically disfavored over the strong metal–hmpa interaction.

Conclusion

With the synthesis and structural characterization of a family of barium thiolates and selenolates, information about an only scarcely explored group of compounds has been obtained. The thiolates can be synthesized in good yield and purity by treating the metals dissolved in ammonia with thiol. The selenolates are accessible by treatment of the metals dissolved in ammonia with diorganodiselenides; this avoids a reduction step that reduces the yield. Addition of various donors to the reaction mixtures, resulted in the formation of compounds that exhibit all modes of ion association in the solid state including contact and separated ions, and an intermediate

with one anion connected to the cation and one separated. The analysis of structure-determining factors provides important information about ligation and solvation processes. By avoiding multidentate donors, a rare, dimeric barium selenolate was obtained. The asymmetric bridging geometry, with one strong, and one weak metal–ligand link indicates the low propensity for the formation of oligomeric systems. The nature of the barium–sulfur and barium–selenium bond was explored by comparing structural features in a family of alkaline earth metal thiolates and selenolates $[\text{M}(\text{thf})_4(\text{EMes}^*)_2]$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$; $\text{E} = \text{S}, \text{Se}$). These compounds display an almost linear *trans* angle for the calcium derivatives, but severe distortion for the barium species. This distortion trend may be explained on the basis of packing effects and/or d-orbital involvement in the small but significant covalent bond contribution, in addition to polarization effects.

Experimental Section

General procedures: All reactions were performed under a purified nitrogen atmosphere by using either modified Schlenk techniques or a Braun Labmaster 100 dry box. Solvents were distilled from Na/K alloy and degassed. Ammonia was predried over sodium metal and condensed into the reaction vessel. Commercially available pyridine and HMPA were stirred over CaH_2 and distilled prior to use. Careful! HMPA has been connected to causing cancer! 18-crown-6 was dissolved in hexanes, refluxed over freshly cut sodium, filtered, and crystallized at -30°C . HSMes^* ,^[22] $\text{Mes}^*\text{SeSeMes}^*$,^[14, 23] and TripSeSeTrip ,^[24] were synthesized according to literature procedures. ^1H and ^{13}C NMR spectra were obtained on a Bruker DPX300 spectrometer. ^{77}Se NMR spectra were attempted, but the low solubility of the compounds did not result in acceptable spectra, even after using THF as the solvent and extended acquisition times. Infrared spectra were recorded as a Nujol mull between NaCl plates with a Perkin–Elmer PE 1600 FT-IR spectrometer. Reliable elemental analyses could not be obtained, even when glove-box handling was attempted, due to the high moisture and oxygen sensitivity of all compounds reported. This is a well-known problem in alkaline earth metal chemistry.^[25] In addition, thiolates and selenolates tend to give notoriously unreliable elemental analyses due to the formation of non-volatile metal selenolates.

Procedure for the synthesis of 1–5: In the glove box, a Schlenk tube was charged with a slight excess of barium metal together with the chalcogenolate source HSMes^* , $\text{Mes}^*\text{SeSeMes}^*$, or TripSeSeTrip . After the addition of freshly distilled THF, the mixtures were cooled to -78°C (dry ice/acetone) and predried ammonia (about 10 mL) were condensed onto the stirred solution to afford deep blue solutions. The solutions were refluxed at -33°C for 4 h (dry ice condenser), followed by gently warming to room temperature, upon which the ammonia evaporated. The remaining solvents were removed in vacuum, resulting in white or pale yellow powders. This residue was redissolved in THF, where appropriate, donors such as 18-crown-6 and HMPA were added, followed by a filtration through a Celite-padded filter frit. Crystals were typically obtained after concentration of the solutions under vacuum and storage of the stock solutions at -20°C .

[Ba(thf)₄(SMes*)₂] \cdot 2THF (1): Reaction conditions: barium (0.14 g, 1 mmol), $(\text{Mes}^*\text{S})_2$ (0.28 g, 0.5 mmol), THF (40 mL), and liquid NH_3 (10 mL), reflux for 4 h at -33°C . The gray residue was mixed with THF (50 mL) and filtered, and the clear, colorless filtrate was stored at -20°C . Colorless rods grew after about 24 h. Yield: 0.34 g (69%); m.p. $112\text{--}115^\circ\text{C}$ (loss of THF), 380°C melts to a brown oil; ^1H NMR (C_6D_6): $\delta = 1.29$ (s, 18H, *para tBu*), 1.40 (m, THF), 1.60 (s, 36H, *ortho tBu*), 3.55 (m, THF) 7.55 (s, 4H, *meta H*); $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_8]\text{THF}$): $\delta =$ (due to very low solubility ipso carbon not observed, even after elongated experiments) 32.00, 32.18, 35.34, 38.75, 126.20, 129.07, 129.83; IR (Nujol): $\tilde{\nu} = 2853$ (s), 1760 (w), 1595 (w), 1286 (s), 1262 (s) 1241 (s), 1212 (s), 1072 (s), 1039 (s), 917 (s), 877 (s), 774 (m), 755 (m), 642 (w), 612 cm^{-1} (w).

[Ba(thf)₄(SeMes*)₂] \cdot 2THF (2): Reaction conditions: barium (0.14 g, 1 mmol), $(\text{Mes}^*\text{Se})_2$ (0.22 g, 0.3 mmol), THF (50 mL), and liquid NH_3 (10 mL), reflux for 4 h at -33°C . The residue was dissolved in THF (40 mL), and the resulting pale yellow solution was stored at -20°C to afford pale yellow crystals in 53% yield (0.17 g). M.p. 255°C (decomposition to a yellow-brown oil); ^1H NMR (C_6D_6): $\delta = 1.28$ (s, 18H, *para tBu*), 1.40 (m, THF) 2.01 (s, 36H, *ortho tBu*), 3.57 (m, THF), 7.55 (s, 4H, *meta H*); $^{13}\text{C}\{^1\text{H}\}$ NMR ($[\text{D}_8]\text{THF}$): $\delta = 32.21, 32.51, 35.27, 39.95, 121.27, 129.20, 142.51, 152.00$; IR (Nujol): $\tilde{\nu} = 3066$ (m), 2073 (w), 1753 (w), 1591 (w), 1541 (w), 1409 (w), 1360 (w), 1282 (w), 1256 (w), 1241 (w), 1212 (w), 1181 (w), 1128 (w), 1074 (w), 1033 (s), 1010 (s), 920 (w), 876 (m), 769 (w), 746 (w), 668 (w), 642 cm^{-1} (w).

[Ba(18-crown-6)(hmpa)₂][(SeMes*)₂] (3): Reaction conditions: barium (0.14 g, 1 mmol) and $(\text{Mes}^*\text{Se})_2$ (0.22 g, 0.30 mmol) in THF (30 mL), and liquid NH_3 (10 mL), refluxed for 4 h at -33°C . The residue was redissolved in THF (40 mL) and filtered, and [18]-crown-6 (0.08 g, 0.3 mmol) and hmpa (1 mL) were added. The reaction mixture was stirred for 1 h and filtered. After removal of solvent (20 mL) and storage at -20°C , crystals grew in 32% yield (0.15 g, 0.11 mmol). M.p. 265°C (decomposition to a dark brown oil); ^1H NMR (C_6D_6): $\delta = 1.46$ (s, 18H, *para tBu*), 2.18 (s, 36H, *ortho tBu*), 2.43 (d, 36H, hmpa), 3.21 (s 24H, crown ether), 7.63 (s, 4H, *meta H*); $^{13}\text{C}\{^1\text{H}\}$ NMR (mixture of $\text{C}_6\text{D}_6/[\text{D}_8]\text{THF}$): $\delta = 31.77, 32.34, 32.87, 33.86, 37.17, 37.21, 70.52, 71.54, 121.24, 123.06, 150.90, 156.87$; IR (Nujol): $\tilde{\nu} = 2853$ (s), 1755 (w), 1583 (w), 1548 (w), 1412 (w), 1350 (w), 1285 (w), 1250 (w), 1238 (w), 1192 (w), 1086 (s), 1017 (w), 977 (w), 956 (w), 920 (w), 875 (w), 831 (w), 821 (w), 757 (w), 748 (w), 638 cm^{-1} (w).

[Ba(py)₃(thf)(SeTrip)₂] (4): Reaction conditions: barium (0.14 g, 1 mmol), $(\text{TripSe})_2$ (0.24 g, 0.43 mmol), THF (40 mL), and liquid NH_3 (10 mL) at -78°C , reflux for 4 h at -33°C . THF (40 mL) and pyridine (0.5 mL, 6.2 mmol) were added, and the mixture was stirred for 2 h. After removal about half of the solvent and storage at -20°C , pale yellow crystals formed over night in 28% yield (0.13 g).

[Ba(18-crown-6)(SeTrip)₂] (5): Reaction conditions: barium (0.14 g, 1 mmol), $(\text{TripSe})_2$ (0.17 g, 0.3 mmol), THF (50 mL), and liquid NH_3 (10 mL), reflux at -33°C for 4 h. The pale yellow residue was dissolved in THF (50 mL), and [18]crown-6 (0.08 g, 0.3 mmol) was added. The reaction mixture was filtered, and the volume of solvent was reduced. Fine pale yellow needles grew over a period of a couple days at -20°C . Yield: 0.19 g, 66%; m.p. 261°C (irreversible to a yellow brown oil); ^1H NMR (C_6D_6): $\delta = 1.35\text{--}1.37$ (d, 24H, *ortho CH*), 1.42–1.44 (d, 12H, *para CH*), 2.93 (sept, 2H, *para CH*), 3.06 (s, 24H, crown ether), 4.57 (sept, 4H, *ortho CH*), 7.04 (s, 4H, *meta H*); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): $\delta = 5.31, 35.21, 35.51, 70.42, 119.57, 140.85, 141.57, 152.03$; IR (Nujol): $\tilde{\nu} = 2360$ (w), 1592 (w), 1548 (w), 1413 (w), 1349 (w), 1284 (w), 1251 (s), 1091 (s), 1057 (w), 1022 (w), 871 (w), 837 (w), 748 (w), 642 (w), 610 cm^{-1} (w).

X-ray crystallographic studies: X-ray quality crystals for all compounds were grown as described above. The crystals were removed from the Schlenk tube under a stream of N_2 and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected under the microscope, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer.^[26] All data sets were collected using a Siemens SMART system, complete with 3-circle goniometer and CCD detector operating at -54°C . The data sets were collected by using a Cryojet low-temperature device from Oxford Instruments and graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The data collections nominally covered a hemisphere of reciprocal space utilizing a combination of three sets of exposures, each with a different ϕ angle, and each exposure covering 0.3° in ω . Crystal decay was monitored by repeating the initial frames at the end of the data collection and analyzing the duplicate reflections. In all cases, no decay was observed. An absorption correction was applied by utilizing the program SADABS.^[27] The crystal structures of all compounds were solved by Direct Methods, as included in the SHELX program package.^[28] Missing atoms were located in subsequent difference Fourier maps and included in the refinement. The structures were refined by full-matrix least-squares refinement on F^2 (SHELX-93).^[28] Hydrogen atoms were placed geometrically and refined by using a riding model, which included free rotation about C–C bonds for methyl groups. Thermal parameters for hydrogen atoms were refined with U_{iso} constrained at 1.2 (for non-methyl groups) and 1.5 (for methyl groups) times U_{eq} of the carrier C atom. The crystallographic programs used for structure refinement and solution were installed on a PC clone and a

Silicon Graphics Indigo² R10000 Solid Impact (SHELX-93). Scattering factors were those provided with the SHELX program system.^[28]

All non-hydrogen atoms, with the exception of some disordered or restrained positions, were refined anisotropically. Disorder was typically handled by including split positions for the affected groups, and included in the refinement with the respective occupancies. Generally, a set of restraints was applied to aid in modeling the disorder. In compounds **1** and **2** a highly disordered solvent molecule was identified. While for the refinement of **2** a disorder model with two half-occupied positions of a THF molecule resulted in a satisfactory description of the electron density, the disorder in **1** was so severe, that the remaining electron density of the solvent molecule was treated by using SQUEEZE (Platon).^[29] The voids in the structure were attributed to a total electron count of 310 electrons, which refers to a THF solvent molecule (40 electrons) on a general position in the space group *I2/a*. The resulting difference Fourier map was symmetrical. A comparative refinement, in which ten maxima were included in the refinement as half-occupied carbon atoms resulted in an asymmetric difference Fourier map. Very comparable *R* values were obtained from the two strategies and no significant differences were detected in the main molecule. In the lattice of compound **5** two THF solvent molecules were found, of which one is described disordered over two positions. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-141602–141606. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgement

This work was supported by Syracuse University, the National Science Foundation (CHE-9702246), and the Deutsche Forschungsgemeinschaft (Postdoctoral stipend for U.E.). Purchase of the X-ray diffractometer was made possible with grants from NSF (CHE-95–27898), the W. M. Keck Foundation and Syracuse University.

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Received: March 21, 2000 [F2374]