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Synthesis and Structure of the Neutral Three-Coordinate Gallium Selenolate Ga[Se(2,4,6-*t*-Bu$_3$C$_6$H$_2$)]$_3$ and the Monomeric Lithium Selenolate Li(THF)$_3$Se(2,4,6-*t*-Bu$_3$C$_6$H$_2$)

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The homoleptic gallium selenolate Ga[Se(2,4,6-*t*-Bu$_3$C$_6$H$_2$)$_3$ has been synthesized by the reaction of GaCl$_3$ with 3 equiv of LiSeMes* (Mes* = 2,4,6-*t*-Bu$_3$C$_6$H$_2$) in toluene. It was characterized by ^{1}H NMR and infrared spectroscopy and by X-ray crystallography. The gallium center has a three-coordinate, almost planar, coordination with Ga–Se bond lengths of nearly 2.324 Å. The precursor lithium selenolate species Li(THF)$_3$SeMes* was also crystallized and structurally characterized. Like its sulfur analogue, it possesses a monomeric structure with the Li center bound to three THF molecules and a selenium in a pseudotetrahedral manner. The Li–Se distance is near 2.57 Å and the LiSeC angle is about 101.9°. Crystal data with Mo Kα (λ = 0.71069 Å) radiation at 130 K: **1**, Ga[Se(2,4,6-t-Bu$_3$C$_6$H$_2$)]$_3$·2PhMe, a = 14.523 (3) Å, b = 14.925 (6) Å, c = 16.651 (3) Å, α = 85.92 (3)°, β = 83.50 (2)°, γ = 61.39 (2)°, Z = 2, triclinic, space group $P\bar{1}$, R = 0.065; **2** Li(THF)$_3$Se(2,4,6-*t*-Bu$_3$C$_6$H$_2$), a = 10.758 (5) Å, b = 18.003 (6) Å, c = 17.954 (5) Å, α = 62.50 (2)°, β = 89.61 (3)°, γ = 87.91 (3)°, Z = 4 (two independent molecules), triclinic, space group $P\bar{1}$, R = 0.054.

Introduction

Relatively few molecular compounds that involve bonds between the heavier main group 3 and 6 elements have been well characterized.[1-14] In view of the potential importance[15] of such compounds as potential precursors to semiconductors, semi-metals, superconductors, photoconductors, or light emitters, the low level of interest is surprising. There is, however, a fairly extensive knowledge of the structures and properties of the binary and ternary chalcogenides of the main group 3 elements.[15] These possess considerable structural diversity, which is exemplified by species such as K$_8$Ga$_4$S$_{10}$·16H$_2$O[16] or TlGaSe$_2$,[17] which have adamantane-like Ga$_4$E$_{10}$ (E = S, Se) units, or by the anion [Se$_2$Ga(μ-Se$_2$Ga)$_5$Se$_2$]$^{10-}$, which has a length of 190 Å,[18] or by the species InGaE$_2$[19] (E = Se, Te), which have edge-sharing layers of GaSe$_4$ or GaTe$_4$ tetrahedra. In addition, the structures of the species Tl$_2$Te$_2^{2-}$ and [In$_2$Se$_2$]$^{4-}$ have been published.[20,21] In contrast, detailed structural information on molecular compounds featuring heavier main group 3 chalcogenide bonds is rare. For example, the structures of only about a half-dozen aluminum or gallium thiolate derivatives are known at present.[6-8] Equally scant are structural data for the heavier derivatives, which are confined to the species [MeSe(AlMe$_3$)$_3$]$^-$,[3] (Me$_2$TlSPh),[4] {TlSSi(O-*t*-Bu)$_3$}$_2$, [Tl(Br)(SPh)$_3$]$^-$,[10a] In(SPh)$_3$py$_2$,[10b] and In(SePh)$_3$[10b] and a small number of polynuclear species such as [Tl$_7$(SPh)$_6$]$^-$ or TlS(*t*-Bu)]$_8$.[12] One of the major reasons for this situation is that the presence of adjacent empty p orbitals and lone pairs in such molecules leads to rapid polymerization and consequent difficulties in their structural characterization.

Recent work in this laboratory has shown that, in main group 3 element compounds, such difficulties may be overcome by using extremely large substituents on the chalcogenide. For example, the compounds M(SMes*)$_3$ (M = Al, Ga; Mes* = 2,4,6-*t*-Bu$_3$C$_6$H$_2$) may be isolated as monomers by treatment of MCl$_3$ with LiSMes*.[22] The extension of this work to a selenium analogue Ga(SeMes*)$_3$ is now described. In addition, the detailed synthesis and characterization of the precursor salt (THF)$_3$LiSeMes* adduct is also reported.

Experimental Section

Starting Materials. GaCl$_3$ (Strem) and *n*-BuLi (1.6 M, hexane) (Aldrich) were obtained commercially and used as received. The selenol HSeMes* was prepared according to literature methods.[23,24]

General Procedures. All experiments were performed either with modified Schlenk techniques or in a Vacuum Atmospheres HE 43-2 drybox under a nitrogen atmosphere. Solvents were freshly distilled from a sodium/potassium alloy and degassed twice prior to use. ^{1}H NMR spectra were recorded in C$_6$D$_6$ or C$_7$H$_8$ solutions by using a General Electric QE 300 spectrometer. Infrared spectra were recorded as Nujol mulls between CsI plates with use of a Perkin-Elmer PE 1430 spectrometer.

Synthesis of Ga[Se(2,4,6-*t*-Bu$_3$C$_6$H$_2$)]$_3$·2PhMe (1). HSeMes* (0.98 g, 3 mmol) was dissolved in toluene (25 mL), and *n*-BuLi (1.9 mL, 3 mmol, 1.6 M solution in *n*-hexane) was added slowly by a syringe at room temperature. The pale yellow solution was stirred for 2 h, during which time the color faded. The solution containing the lithiated selenol was then added dropwise at room temperature to GaCl$_3$ (0.176 g, 1 mmol) dissolved in toluene (25 mL). This gave a pale yellow, turbid solution. The mixture was stirred for a further 18 h and filtered through a Celite-padded glass frit. A reduction of the volume of the filtrate to 15 mL under reduced pressure and storage of the solution at room temperature gave colorless crystals of **1** that were suitable for X-ray structure analysis. Further reduction of the volume to 5 mL gave a total yield of 0.9 g, 87%. The crystal lattice contains two molecules of toluene, which may be removed by keeping the compound for 2 h under reduced (0.01 mm) pressure. Mp: 174–176 °C (decomposition with gas evolution to a yellow oil containing HSeMes*). ^{1}H NMR: δ 7.53 (s, 2 H, *m*-H), 1.66 (s, 18 H, *o*-*t*-Bu), 1.38 (s, 9 H, *p*-*t*-Bu). IR: Ga–Se, ν = 256 cm^{-1}.

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Table I. Selected Crystallographic Data for **1** and **2**[a]

compd	$Ga(SeMes^*)^3 \cdot 2PhMe$ (**1**)	$(THF)_3LiSeMes^*$ (**2**)
formula	$C_{68}H_{103}GaSe_3$	$C_{30}H_{53}LiO_3Se$
fw	1161.9	547.6
color and habit	colorless cubes	colorless parallelpipeds
space group	$P\bar{1}$	$P\bar{1}$
a, Å	14.523 (3)	10.758 (5)
b, Å	14.925 (6)	18.003 (6)
c, Å	16.651 (3)	17.954 (5)
α, deg	85.92 (3)	62.50 (2)
β, deg	83.50 (2)	89.61 (3)
γ, deg	61.39 (2)	87.91 (3)
V, Å^3	3147 (2)	3082 (2)
Z	2	4 (two independent molecules)
d_{calc}, g cm^{-3}	1.226	1.123
μ(Mo Kα), cm^{-1}	20.30	11.20
2θ range, deg	0–55	0–55
no. of obsd reflns, $I > 3\sigma(I)$	7968	6802
no. of variables	619	613
R(F), $R_w(F)$	0.065, 0.075	0.054, 0.066

[a] Data were collected at 130 K with Mo Kα radiation (λ = 0.71069 Å).

Table II. Selected Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for **1** and **2**

	x	*y*	*z*	*U*[a]
Compound **1**				
Ga(1)	3254 (1)	2731 (1)	2464 (1)	23 (1)
Se(1)	4953 (1)	2020 (1)	2860 (1)	26 (1)
Se(2)	1820 (1)	3444 (1)	3425 (1)	29 (1)
Se(3)	2920 (1)	2657 (1)	1145 (1)	27 (1)
C(1)	5612 (5)	1905 (5)	1752 (4)	23 (3)
C(2)	5757 (5)	1118 (5)	1259 (4)	23 (3)
C(6)	5847 (5)	2694 (5)	1434 (4)	24 (3)
C(101)	2653 (5)	3323 (6)	4317 (4)	27 (3)
C(102)	2819 (5)	4170 (5)	4467 (4)	26 (3)
C(106)	3184 (5)	2389 (5)	4731 (4)	22 (3)
C(201)	1403 (5)	3620 (6)	1366 (4)	24 (3)
C(202)	710 (5)	3246 (5)	1673 (4)	22 (3)
C(206)	1086 (6)	4671 (6)	1277 (4)	27 (3)
Compound **2**				
Se(1)	−8668 (1)	−6945 (1)	1666 (1)	26 (1)
Li(1)	−8961 (9)	−6628 (6)	317 (6)	33 (4)
C(1)	−8249 (5)	−7648 (3)	2472 (3)	20 (2)
C(2)	−6979 (4)	−7943 (3)	2632 (3)	21 (2)
C(6)	−9187 (4)	−8236 (3)	2864 (3)	17 (2)
O(1)	−8429 (4)	−7680 (3)	346 (3)	47 (2)
O(2)	−10700 (3)	−6414 (2)	−108 (2)	33 (2)
O(3)	−8167 (3)	−5781 (2)	−678 (2)	39 (2)
Se(2)	−7353 (3)	−6399 (3)	6531 (3)	26 (3)
Li(2)	−6774 (8)	−6483 (5)	5178 (6)	30 (4)
C(19)	−7217 (5)	−7563 (3)	7374 (3)	21 (2)
C(20)	−6056 (5)	−7937 (3)	7772 (3)	21 (2)
C(24)	−8277 (5)	−8080 (3)	7564 (3)	21 (2)
O(4)	−5099 (3)	−6320 (2)	4668 (2)	33 (2)
O(5)	−7659 (3)	−5528 (2)	4290 (2)	34 (2)
O(6)	−7174 (3)	−7547 (2)	5199 (2)	32 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Synthesis of $Li(THF)_3Se(2,4,6\text{-}t\text{-}Bu_3C_6H_2)$ (2). HSeMes* (0.44 g, 1.35 mmol) in THF (30 mL) and *n*-hexane (10 mL) was quantitatively converted into the lithium salt by the dropwise addition of *n*-BuLi (0.85 mL of a 1.6 M hexane solution, 1.35 mmol) at room temperature. The mixture was stirred for 2 h to give a colorless solution. Filtration through Celite followed by a reduction of the volume to 15 mL under reduced pressure and slow cooling to −40 °C gave colorless crystals of **2** suitable for X-ray analysis. Yield: 0.58 g, 79%. Mp: decomposes above 52 °C, giving a white powder that melts at 170 °C, indicating the decomposition of **2** to the selenophenol, mp 172–173 °C.

Table III. Important Bond Distances (Å) and Angles (deg) and Other Structural Parameters for **1** and **2**

Compound **1**			
Ga–Se(1)	2.326 (1)	Se(1)–Ga–Se(2)	119.7 (1)
Ga–Se(2)	2.322 (1)	Se(1)–Ga–Se(3)	122.5 (1)
Ga–Se(3)	2.324 (1)	Se(2)–Ga–Se(3)	117.7 (1)
Se(1)–C(1)	1.960 (7)	Ga–Se(1)–C(1)	94.1 (2)
Se(2)–C(101)	1.966 (8)	Ga–Se(2)–C(101)	95.3
Se(3)–C(201)	1.979 (6)	Ga–Se(3)–C(201)	92.3 (2)
dist of Ga from Se(1), Se(2), Se(3) plane	0.053		
shortest Ga···H dists	2.893, 2.930		
Compound **2**			
Se(1)–Li(1)	2.563 (12)	Li(1)–O(2)	1.982 (10)
Se(2)–Li(2)	2.575 (11)	Li(1)–O(1)	1.935 (12)
Se(1)–C(1)	1.942 (4)	Li(2)–O(4)	1.984 (10)
Se(2)–C(19)	1.938 (4)	Li(2)–O(5)	1.943 (8)
Li(1)–O(1)	1.935 (12)	Li(2)–O(6)	1.961 (12)
Li(1)–Se(1)–C(1)	101.4 (3)	O(2)–Li(1)–O(3)	98.4 (4)
Li(2)–Se(2)–C(19)	102.3 (3)	Se(2)–Li(2)–O(4)	126.0 (5)
Se(1)–Li(1)–O(1)	117.1 (4)	Se(2)–Li(2)–O(5)	104.5 (5)
Se(1)–Li(1)–O(2)	113.7 (5)	Se(2)–Li(2)–O(6)	113.9 (4)
Se(1)–Li(1)–O(3)	115.5 (6)	O(4)–Li(2)–O(5)	99.0 (4)
O(1)–Li(1)–O(2)	105.5 (6)	O(4)–Li(2)–O(6)	100.1 (5)
O(1)–Li(1)–O(3)	104.2 (5)	O(5)–Li(2)–O(6)	112.5 (5)

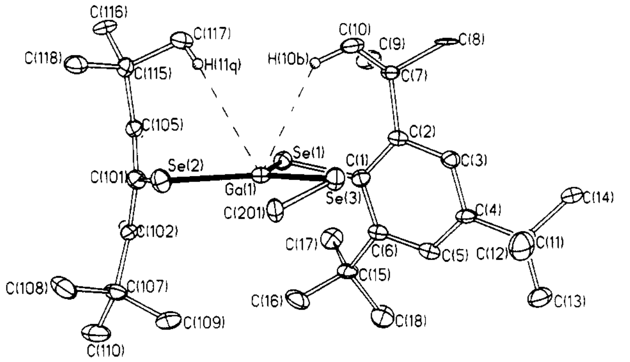

Figure 1. Computer-generated plot of **1** (40% ellipsoids). H atoms and part of the C(201) aromatic ring are omitted for clarity.

X-ray Data Collection, Solution, and Refinement of Structures

The crystals were transferred from the Schlenk tube onto a Petri dish and immediately covered with a layer of hydrocarbon oil. Single crystals were selected, mounted on a glass fiber, and immediately placed in the low-temperature N_2 stream.[25] The X-ray data for compound **1** were collected by using a Syntex $P2_1$ diffractometer equipped with a locally modified Syntex LT-1 device and graphite-monochromated Mo Kα radiation. The data collection for compound **2** was carried out with a Siemens R3 m/V diffractometer, equipped with a locally modified Enraf-Nonius LT apparatus and graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Calculations were performed on a MicroVax Station 3100 using a SHELXTL-PLUS program system (Version 5). Both structures were solved via Patterson synthesis. The atomic form factors, including anomalous scattering factors, were taken from ref 26. An absorption correction was applied by using the method described in ref 27. Table I summarizes the crystal data and refinement for both data collections. Atomic coordinates and isotropic thermal parameters for selected atoms are given in Table II. Important bond distances and angles are presented in Table III.

Results

Syntheses. $Ga(SeMes^*)_3 \cdot 2PhMe$ (**1**) was prepared by the reaction of $GaCl_3$ with 3 equiv of $LiSe(2,4,6\text{-}t\text{-}Bu_3C_6H_2)$ in toluene. The synthesis was performed with the exclusion of donor solvents such as ethers to avoid the formation of metal etherates.

$$GaCl_3 + 3LiSeMes^* \xrightarrow{PhMe} Ga(SeMes^*)_3 \cdot 2PhMe + 3LiCl$$

The THF-solvated species $Li(THF)_3SeMes^*$ was obtained by

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(25) This method is described in: Hope, H. In ACS Symposium Series No. 357; American Chemical Society: Washington, DC, 1987; Chapter 10.

(26) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(27) The absorption correction was made by using the program XABS by H. Hope and B. Moezzi. The program obtains an absorption tensor from $F_o - F_c$ differences: Moezzi, B. Ph.D. Dissertation, University of California, Davis, CA, 1987.

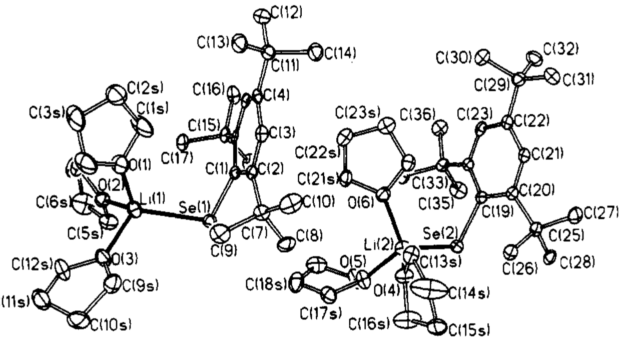

Figure 2. Computer-generated plot of **2** (50% ellipsoids), showing the two independent molecules. H atoms are omitted for clarity.

treatment of HSeMes* dissolved in a 3:1 mixture of THF and *n*-hexane with a solution of *n*-BuLi in hexanes.

$$\text{HSeMes* + } n\text{-BuLi} \xrightarrow{\text{THF}} \text{Li(THF)}_3\text{SeMes* + } n\text{-BuH}$$

Structural Descriptions. Ga[Se(2,4,6-*t*-Bu$_3$C$_6$H$_2$)]$_3$·2PhMe (1). The X-ray structure of Ga(SeMes*)$_3$·2PhMe consists of discrete, neutral molecules of Ga(SeMes*)$_3$ with no imposed crystallographic symmetry. The molecular structure is given in Figure 1. Important bond lengths and angles are given in Table III. The compound has an almost trigonal-planar GaSe$_3$ core with deviations of up to 2.5° from idealized 120° angles at Ga. The geometry at Ga is almost planar, and the sum of the angles at gallium is 359.9 (2)°, with the gallium atom located 0.053 Å above the Se$_3$ plane. The gallium–selenium distances are quite uniform and average 2.324 (2) Å. The average Se–C distance is 1.967 (8) Å, and the angles between the Se(1)Se(2)Se(3) plane and the aromatic rings are 83.2, 84.2, and 87.7°, respectively. The ipso carbons are located 0.4702, 0.1676, and 0.4106 Å from the plane of the selenium atoms. The angles between the Se–C bonds and this plane are 13.9, 4.9, and 12.0°. In addition, there are angles of 17.1, 15.5, and 17.3° between the Se(1)–C(1), Se(2)–C(101), and Se(3)–C(201) vectors and the averaged plane of their respectively aromatic rings. The shortest Ga···H distances are 2.839 Å (H(11q)) and 2.930 Å (H(10b)), which are associated with the C(1) and C(101) rings. No distortions in the geometries of the relevant *t*-Bu groups were observed. One of the *p*-*tert*-butyl groups is disordered, and it was refined with equal occupancy at two positions. Each asymmetric unit contains two toluene molecules, one of which is disordered and could not be modeled satisfactorily.

Li(THF)$_3$SeMes* (2). This structure is illustrated in Figure 2. Important bond distances are given in Table III. The unit cell contains two crystallographically independent, but chemically identical, molecules of formula Li(THF)$_3${Se(2,4,6-*t*-Bu$_3$C$_6$H$_2$)} with no imposed crystallographic symmetry. The Li–Se distances are 2.563 (12) and 2.575 (11) Å, and the Se(1)–C(1) distances are 1.942 (4) and 1.938 (4) Å with angles of 101.4 (3) and 102.3 (3)° at Se. The average Li–O distance is near 1.96 (1) Å. The Li$^+$ ion is bound in a distorted tetrahedral fashion to three oxygens and the selenium; however, the angles at Li in the two independent molecules are quite different. A comparison of the Se–Li–O angles show a range from 113.7 to 117.1° at Li(1) and a much larger range from 104.5 to 126.0° at Li(2).

Discussion

Thiolate, selenolate, and tellurolate derivatives of the elements Al–Tl are a relatively poorly investigated family of compounds. For example, there are only a handful of structures known for aluminum and gallium thiolates, which are, at present, the best studied species.[6–8,22] Structural data for selenolate compounds of these elements are almost completely unknown. Very few such compounds have been characterized. The known examples are limited to the species Me$_2$GaSeMe, Me$_2$GaSePh[1] (and their complexes with NMe$_3$), Et$_2$GaSeSiEt$_3$,[2] and K[MeSe(AlMe$_3$)$_3$]·2C$_6$H$_6$.[3] The former compounds are dimeric in organic solvents, and in the case of the NMe$_3$ adducts, which are monomeric, the NMe$_3$ may be removed by pumping at room temperature. The ion [MeSe(AlMe$_3$)$_3$]$^-$ features Se bound to three AlMe$_3$ groups and a methyl group with Al–Se distances that span the range 2.566 (5)–2.594 (6) Å.[3] In a broader context there is considerable current interest in the differences between selenolato and thiolato metal complexes. A major reason for this is the involvement of selenium as selenocysteine residues in biological systems,[28] the importance of which is not clearly understood and is under investigation.[29] The unique properties of selenium metal coordination is thus of significant interest.

Recent results in this laboratory have shown that it is possible to synthesize neutral homoleptic and monomeric thiolate derivatives of aluminum and gallium by using the very bulky thiolate ligands [S(2,4,6-*t*-Bu$_3$C$_6$H$_2$]$^-$ ([SMes*]$^-$).[22] The size of this ligand prevents the association normally found in metal thiolates[30] and generally allows facile characterization of the product. For reasons stated in the Introduction, it was desirable to investigate the corresponding selenium derivatives. The reaction between LiSeMes*, generated in situ, and GaCl$_3$ proceeded to give **1** in good yield. The crystals of Ga(SeMes*)$_3$, which were obtained from toluene solution, were not isomorphous with their sulfur counterpart Ga(SMes*)$_3$ owing to the inclusion of two toluenes in the lattice. It is not clear what subtleties in the crystallization process led to these differences. It is known, however, that in closely related systems (e.g. the T-shaped zinc species [Et$_2$OZn(SMes*)$_2$)][31]) the molecular structure and packing are intimately connected. Thus, apparently small changes, such as in the Ga–E–C angles (E = S, 100.4°,[22] E = Se, 93.9°) or in the average angle between the E–C bond and the plane of the aromatic ring (11.6° in the case of Ga(SMes*)$_3$[22] and 17° for Ga(SeMes*)$_3$), may have considerable influence on packing efficiency. A further relevant point concerns the distance of the ipso carbons from the Se$_3$ plane and the average angle between the aromatic ring planes and the Se$_3$ plane. For the latter parameter the angles are nearly the same in both compounds ~85° in **1** and ~82° in its sulfur analogue. In contrast, the ipso carbons in **1** deviate an average of about 0.35 Å from the Se$_3$ plane, whereas, in the sulfur compound, the corresponding average deviation is ~0.62 Å. Another way of measuring this difference is by using the average angle between the S–C or Se–C bonds and the S$_3$ and Se$_3$ planes. In the case of **1** the angle averages ~10.3° whereas for the sulfur species the average is 20.5°. The difference between the two compounds is probably due to the greater crowding in the sulfur species owing to the shorter Ga–S bond. In addition, the variation in this parameter indicates that the interaction between the sulfur or selenium lone pairs and the p orbital on gallium is probably minor.

The differences described above aside, the structures of Ga(SeMes*)$_3$ and its sulfur analogue are broadly similar. The gallium atom is bound to three equivalent -SeMes* groups. Thus, **1** is one of a small, but growing, number of three-coordinate gallium compounds.[22,32–36] There is a slight deviation of the Ga center from strict planarity. This may be a consequence of a weak

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interaction between one or more hydrogens from an *o-tert*-butyl group or of the ionic character of the Ga–Se bonds. The bending of the planes of the aromatic rings toward the metal was also observed in the sulfur analogue.[22] This is contrary to what is expected on steric grounds and may be a consequence of packing forces in which the rings of neighboring molecules have a tendency to stack parallel to each other. The weak interaction between some of the *o-tert*-butyl hydrogens and the Ga center may also be partly responsible for these distortions. The Ga–Se bonds average 2.324 (1) Å. This value may be compared to the length of the 2.442 (2) Å observed at the bridging Se in the $GaSe_4$ tetrahedra in $InGaSe_2$[19] and 2.43 and 2.35 Å for the bridging and terminal Ga–Se bonds in the Ga_4Se_{10} units in $TlGaSe_2$.[17] The Ga–Se distance in **1** is also somewhat less than the sum of the ionic radii 2.4 Å.[36] The short Ga–Se distance in **1** is probably due to the low coordination number of gallium and perhaps some ionic character in the Ga–Se bond. The low average angle ~93.9° at the seleniums is a characteristic feature of divalent selenium and is essentially unaffected by the very crowded nature of the molecule. The IR spectrum of **2** displays a band of medium intensity at 256 cm^{-1}, which is attributable to the Ga–Se stretching frequency. The single Ga–Se band is also consistent with the approximate C_{3h} symmetry in **1**. Oddly, the stretching frequency of the Ga–Se bonds is very close to the 261 cm^{-1} observed for the species $i\text{-}Pr_2GaSeEt$[14] that probably has bridging selenolate ligands.

The most notable feature of the structure of the lithium salt **2** is its monomeric formulation. The structure of **2** also appears to be the first complete description for an alkali-metal salt of a selenolate although Li–Se bond lengths of 2.6 (1) and 2.7 (1) Å have been reported for the bridged species $[(\eta^5\text{-}C_5H_5)_2Lu(\mu\text{-}SePh)_2Li(THF)_2]$.[38] In addition, some structural parameters (Li–Se = 2.573 Å and Li–Se–C = 103°) were described for a species of formula $Li(THF)_nSeMes^*$ in a conference report, but no other details were provided.[39] There is no doubt, however, that **2** resembles its sulfur analogue[40] quite closely, and the crystals of the compounds are isomorphous. It also appears to be similar to the structure of the tellurium analogue,[39] which was partially described in a recent report and has a Li–Te distance of 2.82 (1) Å.[41] The monomeric formulation for **2** and its sulfur analogue is probably to the relatively weak coordination of sulfur or selenium donors for Li^+. This weakness discourages bridging, and in the presence of donor solvents such as THF, a monomeric structure is observed. The size of the Mes* substituent also favors the monomeric structure, although it is notable that the corresponding aryloxy salt $[(THF)LiOMes^*)]_2$ is dimeric,[42] presumably because of stronger Li–O bonding. The Li–Se–C angles, 101.4 (3) and 102.3 (3)°, are close to, but slightly narrower than, the corresponding angles in the sulfur compound, which are 103.1 (3) and 104.5 (3)°. The wider M–E–C angles for the lithium salts, in comparison to those observed for the gallium thiolato and selenolato species, may be due to the more ionic nature of the Li–S and Li–Se bonds. The lower degree of orbital overlap presumably results in less stringent directional requirements for the bonds. Further evidence for this viewpoint comes from the recently reported structures[41] $[(TMEDA)_2NaTeMes]$ and $[(18\text{-crown-}6)\text{-}KTe(2,4,6\text{-}i\text{-}Pr_3C_6H_2)]$, which have angles of 102.26 (5) and 77.68 (7)° at tellurium. The Li–Se distances in **1**, 2.57 (1) Å, are about 0.12 Å longer than those seen in the sulfur derivative. This difference is practically identical with the bond length differences observed for $Ga(EMes^*)_3$ (E = S, Se). Compound **1** is not very thermally stable. In the Experimental Section it was noted that it decomposes at 52 °C in the melting point tube. In reality, the compound slowly decomposes in solution at ambient temperature and should be used as soon as possible after it is generated.

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Supplementary Material Available: Full tables of data collection and details of refinement, atomic coordinates and isotropic thermal parameters, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters (19 pages); tables of structure factors (96 pages). Ordering information is given on any current masthead page.

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