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Compounds with M$_3$Se$_3$ (M = Li, Zn) Rings: Synthesis and Characterization of [Zn(CH$_2$SiMe$_3$)Se-2,4,6-*t*-Bu$_3$C$_6$H$_2$]$_3$·0.5C$_6$H$_{14}$ and [Li(THF)Se-2,4,6-*t*-Bu$_3$C$_6$H$_2$]$_3$·PhMe

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The synthesis and structural characterization of two six-membered ring species containing selenium are described. The compound [Zn(CH$_2$SiMe$_3$)SeMes*]$_3$·0.5 C$_6$H$_{14}$ (Mes* = 2,4,6-*t*-Bu$_3$C$_6$H$_2$), (**1**) was synthesized by the reaction Zn(CH$_2$SiMe$_3$)$_2$ with 1 equiv of HSeMes* in hexane whereas [Li(THF)SeMes*]$_3$·PhMe (**2**) was obtained by the lithiation of HSeMes* with *n*-BuLi in the presence of 1 equiv of THF. Each molecule has an M$_3$Se$_3$ core (M = Li, Zn) structure. Unlike the corresponding sulfur species, **1** has a nonplanar Zn$_3$Se$_3$ array and represents the first structure of this type for a selenium compound. The nonplanar Li$_3$Se$_3$ core in **2** involves pyramidal coordination at selenium and almost planar lithium coordination. Both species were characterized by ^{1}H NMR and IR spectroscopy and X-ray crystallography. Crystal data with Mo Kα (λ = 0.710 69 Å) at 130 K are as follows: **1**, *a* = 10.355(5) Å, *b* = 18.850(8) Å, *c* = 20.885(8) Å, α = 83.67(3)°, β = 86.92(4)°, γ = 77.62(4)°, V = 3956(3) Å^3, *Z* = 2, space group $P\bar{1}$, 7550 ($I > 3\sigma(I)$) data, *R* = 0.077; **2**, *a* = 9.973(5) Å, *b* = 18.466(7) Å, *c* = 21.735(9) Å, α = 74.26(3)°, β = 79.45(4)°, γ = 78.21(2), V = 3725(3) Å^3, *Z* = 2, space group $P\bar{1}$, 5357 ($I > 2\sigma(I)$) data, *R* = 0.069.

Introduction

Structural data for selenolate compounds of zinc and lithium are very rare. Molecular structures that feature Zn–Se bonds are limited to Zn(dsec)$_2$ (dsec = diethyldiselenocarbamate),[1] [Na(15-crown-5)]$_2$[Zn(Se$_4$)$_2$],[2] [PPh$_4$]$_2$[Zn(SePh)$_4$],[3] [PPh$_4$]$_2$[Zn(Se$_4$)$_2$],[4,5] [PPh$_4$]$_2$[Zn(CSe$_4$)$_2$],[6] [PPh$_4$]$_2$[Zn(C$_3$Se$_5$)$_2$],[6] ZnSe$_4$(*N*-MeIm)$_2$,[7] [Zn(SeMes*)$_2$-*p*-OCHC$_6$H$_4$OMe]$_2$,[8] and [PPh$_4$]$_6$[Zn(Se$_4$)$_2$]$_2$[WSe$_4$]·DMF.[9] A feature of these compounds is that zinc is always found in the coordination number 4. The number of well-characterized lithium salts of selenolates is even more limited than those of zinc. At present only two structures, Li(THF)$_3$SeMes*[10,11] (Mes* = 2,4,6-*t*-Bu$_3$C$_6$H$_3$) and [Li(DME)SeSi(SiMe$_3$)$_3$]$_2$[12] have been determined. This research group became interested in both these classes of compound and related species for a number of reasons. In the case of the zinc compound **1**,it is part of a growing class of six-membered rings which can, in some instances, display stabilization or structural properties consistent with some delocalization of their three nonbonded electron pairs into π-orbitals. Among these are species such as [MesBP(C$_6$H$_{11}$)]$_3$,[13] [MeAlN(2,6-*i*-Pr$_2$C$_6$H$_3$)]$_3$,[14] [GeN(2,6-*i*-Pr$_2$C$_6$H$_3$)]$_3$,[15] or [Zn(CH$_2$SiMe$_3$)SMes*]$_3$,[16] which display planar or near planar ring structures and short bond distances within the ring. For the lithium derivative **2**, a trimeric formulation is a fairly rare structural motif. For chalcogenide ligands, known examples are limited to recently reported oxygen derivatives [LiO{4-Me-2,6(CHN-*i*-Pr$_2$)$_2$C$_6$H$_2$}]$_3$,[17] [LiOSi(*t*-Bu)OSi(t-Bu)$_2$F]$_3$,[18] and [LiOC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4]$_3$,[19] which possess chelate structures. Trimeric structures are unknown for lithium salts of the heavier organochalcogenides. This paper describes the synthesis and characterization of two novel six-membered ring species. These are [Zn(CH$_2$SiMe$_3$)SeMes*]$_3$, **1**, which has a distorted, nonplanar, hexagonal array of alternating Zn and Se atoms and [Li(THF)SeMes*]$_3$, **2**, whose six-membered Li$_3$Se$_3$ ring features nonplanar coordination at lithium and selenium.

Experimental Section

General Procedures. All reactions were performed under N$_2$ by using either modified Schlenk techniques or a Vacuum Atmospheres HE43-2 drybox. *n*-Hexane was freshly distilled from a Na/K alloy and degassed two times before use. Commercially available ZnCl$_2$ and ClCH$_2$SiMe$_3$ were used as received. The compounds Zn(CH$_2$SiMe)$_2$[20] and HSe-2,4,6-*t*-Bu$_3$C$_6$H$_2$[21,22] were synthesized by literature procedures. ^{1}H and ^{77}Se NMR spectra were obtained near 300 and 57.3 MHz in C$_6$D$_6$ on a GE QE-300 spectrometer with C$_6$D$_6$ and (PhSe)$_2$ as standards. Infrared spectra were recorded as a Nujol mull between CsI plates, using a Perkin-Elmer PE 1430 spectrometer.

Synthesis of [Zn(CH$_2$SiMe$_3$)SeMes*]$_3$·0.5C$_6$H$_{14}$, 1. Zn(CH$_2$SiMe$_3$)$_2$ (0.65 g, 2.71 mmol) was dissolved in *n*-hexane (10 mL) and treated with a solution of HSeMes* (0.88 g, 2.71 mmol) in hexane (30 mL). The reaction mixture became yellow with concomitant SiMe$_4$ evolution. The solution was allowed to stir overnight at room temperature. After the filtration through a Celite-padded filter frit and reduction of the volume to *ca.* 5 mL, colorless crystals were obtained: Yield 1.1 g, 83%; mp 185–187 °C dec. Anal. Calcd for C$_{66}$H$_{120}$Se$_3$Si$_3$Zn$_3$ (without 0.5 equiv

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Table I. Summary of Data Collection, Structure Solution, and Refinement of $[Zn(CH_2SiMe_3)SeMes^*]_3 \cdot 0.5C_6H_{14}$ (**1**) and $[Li(THF)SeMes^*]_3 \cdot PhMe$ (**2**)[a]

	1	**2**
formula	$C_{69}H_{127}Se_3Si_3Zn_3$	$C_{73}H_{119}Li_3O_3Se_3$
fw	1476.4	1302.4
cryst shape	colorless rods	colorless needles
cryst size, mm	1.2 × 0.4 × 0.45	0.08 × 0.12 × 1.1
a, Å	10.355(5)	9.973(5)
b, Å	18.850(8)	18.466(7)
c, Å	20.885(8)	21.735(9)
α, deg	83.67(3)	74.26(3)
β, deg	86.92(4)	79.45(4)
γ, deg	77.62(4)	78.21(3)
V, Å^3	3956(3)	3725(3)
Z	2	2
space group	$P\bar{1}$	$P\bar{1}$
d_{calc}, g/cm^3	1.22	1.16
linear abs coeff, cm^{-1}	23.6	15.2
2θ range, deg	0–55	0–44
no. of obsd reflcns	7550 ($I > 3\sigma(I)$)	5357 ($I > 2\sigma(I)$)
no. of variables	688	709
R, R_w	0.077, 0.080	0.069, 0.065

[a] Data were collected at 130 K using a Siemens R3m/V diffractometer with monochromated Mo Kα radiation.

Table II. Important Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[Zn(CH_2SiMe_3)SeMes^*]_3 \cdot C_6H_{14}$ (**1**) and $[Li(THF)SeMes^*]_3 \cdot PhMe$ (**2**)

atom	x	y	z	U_{iso}
		Compound **1**		
Se(1)	6619(1)	1335(1)	2286(1)	25(1)
Se(2)	4036(1)	2648(1)	3065(1)	23(1)
Se(3)	3714(1)	2686(1)	1338(1)	23(1)
Zn(1)	5662(1)	1521(1)	3358(1)	25(1)
Zn(2)	3096(1)	3520(1)	2171(1)	23(1)
Zn(3)	5628(1)	1667(1)	1231(1)	36(1)
Si(1)	7268(2)	606(1)	4645(1)	46(2)
Si(2)	539(2)	4891(1)	1902(1)	32(1)
Si(3)	7420(2)	864(1)	31(1)	40(1)
C(1)	7822(8)	382(5)	2361(5)	19(4)
C(101)	3857(8)	3024(6)	3917(4)	21(4)
C(201)	3985(8)	3128(5)	459(4)	16(3)
C(301)	5758(9)	1121(7)	4250(5)	34(4)
C(401)	2076(8)	4495(6)	2329(5)	25(4)
C(501)	5801(9)	1283(9)	375(6)	61(7)
		Compound **2**		
Se(1)	7340(1)	1144(1)	7718(1)	28(1)
Se(2)	10646(1)	6551(1)	6500(1)	31(1)
Se(3)	7884(1)	5005(1)	7408(1)	35(1)
Li(1)	6968(18)	5810(4)	8184(6)	45(8)
Li(2)	9364(13)	7590(7)	6990(8)	37(8)
Li(3)	9846(14)	5343(7)	6565(8)	51(9)
O(1)	5508(8)	5665(4)	8881(3)	49(4)
O(2)	9914(7)	8554(3)	6809(3)	44(3)
O(3)	11012(8)	4735(4)	6035(3)	56(4)
C(1)	7048(8)	7955(4)	8183(4)	21(4)
C(19)	11765(7)	7140(4)	5764(3)	22(4)
C(37)	8854(9)	3946(3)	7659(4)	24(4)

of *n*-hexane): C, 55.4; H, 8.4. Found: C, 55.5; H 8.51. ^{1}H NMR (C_6D_6) (δ): 7.51 (s, 2H, *m*-H); 1.78 (s, 18H, O-*t*-Bu), 1.28 (s, 9H), *p*-*t*-Bu); –0.14 (s, 9H, $SiMe_3$); –0.48 (s, 2H, (CH_2). ^{77}Se NMR (C_6D_6): 514.5. IR (cm^{-1}): 1591 m, 1578 sh, 1473 sh, 1410 st, 1402 st, 1372 st, 1358 st, 1255 m, 1242 st, 1209 w, 1198 sh, 1175 w, 1166 w, 1090 br, 1010 m, 948 m, 895 w, 871 m, 852 m, 822 m, 802 m, 742 m, 720 m, 712 m, 690 w, 680 w, 592 w, 608 w, 557 w, 528 2, 382 m.

Synthesis of $[Li(THF)SeMes^*]_3 \cdot PhMe$, 2. Freshly reduced HSeMes* (1.11 g, 3.41 mmol) was dissolved in toluene (30 mL), and the solution was cooled with an ice bath to 0 °C. The pale yellow solution was treated with *n*-BuLi (2.13 mL of a 1.6 M solution in hexanes, 3.4 mmol) and THF (0.25 mL). The solution became colorless and was stirred for 16 h at ambient temperature. After a reduction of the volume to *ca.* 10 mL and storage of the solution in a –20 °C freezer, large colorless crystals of **2** were obtained. The crystals decompose rapidly upon their removal from the mother liquor: Yield 0.85 g, 67%; mp dec >130 °C. Anal. Calcd for $C_{73}H_{119}Li_3O_3Se_3$: C, 67.32; H, 9.22. Found: C, 56.41; H, 8.71. ^{1}H NMR (C_6D_6) (δ): 7.51 (s, 2H, *m*-H), 3.08 (m, 4H, THF), 2.05 (s, 18H, *o*-*t*-Bu), 1.31 (s, 9H, *p*-*t*-Bu), 1.038 (m, 4H, THF). ^{77}Se NMR: (C_6D_6) (δ): 57.88. IR (cm^{-1})1588 w, 1568 sh, 1538 w, 1473 sh, 1462 st, 1460 st, 1452 st, 1442 st, 1408 w, 1375 st, 1362 sh, 1345 sh, 1235 w, 1209 w, 1173 w, 1152 w, 1138 m, 1018 m, 918 w, 888 w, 874 m, 800 w, 748 m, 710 w, 640 w, 410 br, m, 372 br, m.

X-ray Crystallographic Studies. The crystals were removed from the Schlenk tube under a stream of N_2 and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream as described in ref 23. Compounds **1** and **2** were collected at 130 K with the use of a Siemens R3m/V diffractometer (Mo Kα radiation λ = 0.710 69 Å) equipped with a graphite monochromator and a locally modified Enraf-Nonius Universal low-temperature device for low temperature work. Crystallographic programs used for the structure solutions and refinements were those of SHELXTL-Plus[24] installed on a MicroVax station 3200. Scattering factors were from common sources.[25] An absorption correction was applied using the method described in ref 26. Some details of data collection and refinement are given in Table I, and coordinates for selected atoms are given in Table II. Important bond distances and angles are provided in Table III. Further details are provided in the supplementary material.

The crystal structures of **1** and **2** were solved by Patterson synthesis; missing atoms were located on a difference map in several different Fourier cycles. The crystal structures were refined by full matrix least squares refinement. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement at calculated positions using a riding model with C–H = 0.96 Å and U_H = 0.05 U_C.

Results and Discussion

Structural Descriptions. $[Zn(CH_2SiMe_3)SeMes^*]_3 \cdot 0.5C_6H_{14}$, 1. The structure of **1** is presented in Figure 1, and it consists of neutral, discrete, trimers with no crystallographically imposed symmetry. The zinc atoms have distorted trigonal planar coordination whereas the coordination at the selenium centers display varying pyramidicity as indicated by the following angle sums ($\Sigma°$) at the seleniums: $\Sigma°$Se(1) = 350.3°, $\Sigma°$Se(2) = 357.6°, $\Sigma°$Se(3) = 340.6°. The Zn–Se bond lengths range from 2.429(2) to 2.467(2) Å. The average Zn–C distance is 1.95(2) Å, and the Se–C distances average 1.96(2) Å. The six-membered Zn_3Se_3 ring shows significant deviations from planarity as illustrated in Figure 2, which also shows the distance of the ring atoms from the calculated least-squares plane.

$[Li(THF)SeMes^*]_3 \cdot PhMe$, 2. The structure of **2**, which is illustrated in Figure 3, consists of neutral, well separated trimeric units with no crystallographically imposed symmetry. The core consists of a six-membered ring comprised of alternating lithium and selenium atoms. These ring atoms have the configuration depicted in Figure 4. The lithiums display almost planar trigonal coordination with the only significant deviation involving Li(1) where $\Sigma°$Li(1) = 355.0°. The coordination at the selenium centers display greater pyramidicity with angle sums of 348.2°, 353.0°, and 333.2° for Se(1), Se(2), and Se(3). The mean deviation of the ring atoms from the least-squares plane of the Li_3Se_3 ring is 0.34 Å. The Li–Se bond length ranges from 2.462(13) to 2.478(14) Å, the average Se–C bond length is 1.97 Å, and the Li–O distances range from 1.888(14) to 1.903(16) Å.

Discussion

Compounds **1** and **2** were synthesized in good yields in a straightforward manner. The zinc species **1** was obtained by treatment of the readily synthesized $Zn(CH_2SiMe_3)_2$[20] with 1

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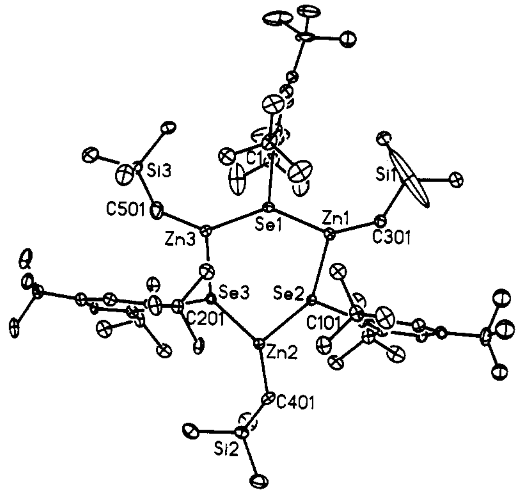

Figure 1. Computer-generated plot of **1** (35% ellipsoids). Hydrogen atoms are omitted for clarity.

Table III. Important Bond Lengths (Å) and Angles (deg) of $[Zn(CH_2SiMe_3)SeMes^*]_3 \cdot 0.5C_6H_{14}$ (**1**) and $[Li(THF)SeMes^*]_3 \cdot PhMe$ (**2**)

Compound 1			
Bond Lengths			
Se(1)–Zn(1)	2.429(2)	Se(2)–Zn(3)	2.442(2)
Se(2)–Zn(1)	2.452(2)	Se(2)–Zn(2)	2.443(2)
Se(3)–Zn(2)	2.440(2)	Se(3)–Zn(3)	2.467(2)
Se(1)–C(1)	1.950(8)	Se(2)–C(101)	1.97(1)
Se(3)–C(201)	1.961(8)	Zn(1)–C(301)	1.93(1)
Zn(2)–C(401)	1.97(1)	Zn(3)–C(501)	1.99(1)
Si(1)–C(301)	1.84(1)	Si(2)–C(401)	1.839(9)
Si(3)–C(501)	1.84(1)		
Bond Angles			
Zn(1)–Se(1)–Zn(3)	130.4(1)	Se(1)–Zn(1)–Se(2)	97.7(1)
Zn(1)–Se(1)–C(1)	106.4(3)	Se(1)–Zn(1)–C(301)	143.6(3)
Zn(3)–Se(1)–C(1)	113.5(3)	Se(2)–Zn(1)–C(301)	118.7(3)
Zn(1)–Se(2)–Zn(2)	144.7(1)	Se(2)–Zn(2)–Se(3)	96.1(1)
Zn(1)–Se(2)–C(101)	97.2(3)	Se(2)–Zn(2)–C(401)	120.6(3)
Zn(2)–Se(2)–C(101)	115.7(3)	Se(3)–Zn(2)–C(401)	142.9(3)
Zn(2)–Se(3)–Zn(3)	131.1(1)	Se(1)–Zn(3)–Se(3)	107.7(1)
Zn(2)–Se(3)–C(201)	116.8(3)	Se(1)–Zn(3)–C(501)	138.2(4)
Zn(3)–Se(3)–C(201)	92.7(2)	Se(3)–Zn(3)–C(501)	113.7(3)
Compound 2			
Bond Lengths			
Se(1)–Li(1)	2.473(9)	Se(3)–Li(1)	2.476(12)
Se(1)–Li(2)	2.462(13)	Se(3)–Li(3)	2.478(14)
Se(1)–C(1)	1.972(9)	Se(3)–C(37)	1.974(6)
Se(2)–Li(2)	2.463(14)	Li(1)–O(1)	1.902(16)
Se(2)–Li(3)	2.478(14)	Li(2)–O(2)	1.888(14)
Se(2)–C(19)	1.972(7)	Li(3)–O(3)	1.903(16)
Bond Angles			
Li(1)–Se(1)–Li(2)	127.4(4)	Se(1)–Li(1)–Se(3)	111.8(5)
Li(1)–Se(1)–C(1)	126.7(4)	Se(1)–Li(1)–O(1)	115.5(5)
Li(2)–Se(1)–C(1)	94.1(4)	Se(3)–Li(1)–O(1)	127.7(6)
Li(2)–Se(2)–Li(3)	126.1(4)	Se(1)–Li(2)–Se(2)	108.5(5)
Li(2)–Se(2)–C(19)	99.6(4)	Se(1)–Li(2)–O(2)	128.1(7)
Li(3)–Se(2)–C(19)	127.3(5)	Se(2)–Li(2)–O(2)	123.4(6)
Li(1)–Se(3)–Li(3)	119.4(5)	Se(2)–Li(3)–Se(3)	116.7(6)
Li(1)–Se(3)–C(37)	123.2(4)	Se(2)–Li(3)–O(3)	114.0(7)
Li(3)–Se(3)–C(37)	90.6(3)	Se(3)–Li(3)–O(3)	128.6(7)

equiv of HSeMes*[21,22] with concomitant elimination of $SiMe_4$. This type of elimination, involving a zinc dialkyl, is one of the oldest known classes of organometallic reactions.[27] The lithium derivative **2** can be isolated if only 1 equiv of THF per lithium is employed during the addition of *n*-BuLi.

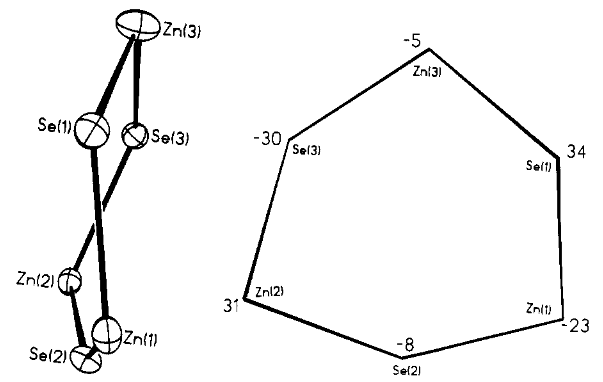

Figure 2. Computer-generated plot of the ring framework of **1** showing the deviations from planarity (in units of 0.01 Å) relative to the least-squares plane.

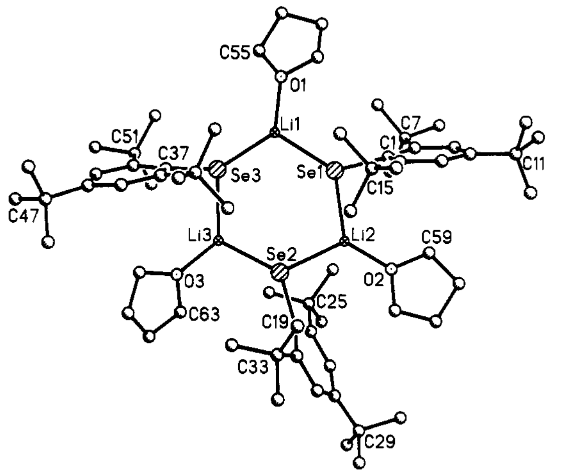

Figure 3. Computer-generated plot of **2** (35% ellipsoids). Hydrogen atoms are omitted for clarity.

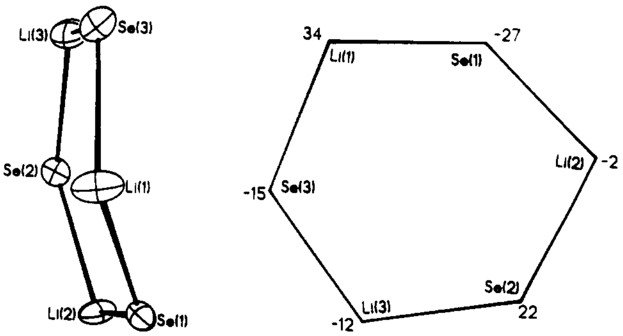

Figure 4. Computer-generated plot of the ring framework of **2** showing the deviations from the least-squares plane in units of 0.01 Å.

The structure of **1** may be compared with the related sulfur analogue $[Zn(CH_2SiMe_3)SMes^*]_3$. The crystals of the two molecules are not isomorphous and the major difference between the two compounds involves the conformation of the Zn_3E_3 (E = S, Se) rings. The selenium geometries are more pyramidal (average $\Sigma°Se = 349.5°$) than the sulfurs (average $\Sigma°S = 356.3°$). Moreover, the Zn_3Se_3 has a twist structure (Figure 2) that the Zn_3S_3 ring does not, to any great extent, possess. The average Zn–Se distance is 2.45 Å *vs* 2.33 Å found in the corresponding Zn–S compound. Both distances are longer than the sum of the covalent radii of Zn (1.2 Å) and S (1.02 Å) or Se (1.17 Å). These values predict distances of 2.22 Å for Zn–S and 2.37 Å for Zn–Se. However, it should be borne in mind that, in **1** and its zinc analogue, the chalcogenide ligands are bridging and longer bond lengths are to be expected. The Zn–Se bond lengths in **1** may be compared to those recently reported in the adduct $[Zn(SeMes^*)_2(p\text{-}O{=}CHC_6H_4OMe)]_2$.[8] This compound has a dimeric

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[27] Frankland, E. *Jahresber. Fortschr. Chem. Verw. Thiele Anderer Wiss.* **1857**, 418.

structure with bridging and terminal –SeMes* groups. The zinc atoms are each coordinated by an aromatic aldehyde. Significantly, the Zn–Se bridging distances average about 2.5 Å long. Presumably, the difference between this value and that observed in **1** is a consequence of the higher coordination number (4) at Zn. On the other hand, the Zn–Se distance for the terminal –SeMes* group is only 2.345(3) Å. Similarly, quite short Zn-S bonds (average Zn–S distance 2.196(2) Å) are observed in the species $(Et_2O)Zn(SMes^*)_2$,[28] which also features terminal –SMes* groups.

An interesting aspect of the structure of **1** and its sulfur analogue is that both of these rings possess a total of six nonbonded electrons in the lone pairs of the chalcogenides. This has led to some speculation[16,29] on the possible delocalization of these electrons in a quasiaromatic system derived from six ring p-orbitals. The near planarity of the zinc–sulfur system (especially when contrasted with the structure of the dimer $[Zn(CH_2SiMe_3)SCPh_3]_2$[16] in which the sulfurs are strongly pyramidal) and the relatively short Zn–S bonds have suggested, if not proven, some tendency to delocalize.[29] However, owing to the more pyramidal nature of the seleniums and the twist structure of the Zn_3Se_3 ring there is no suggestion of delocalization in **1**. Most probably, the larger inversion barrier at selenium in comparison to sulfur combined with reduced steric requirements of **1** (owing to the longer Zn–Se and Se–C bonds) is responsible for the observed structure.

The lithium selenolate species **2** constitutes a new type of structure for lithium derivatives of the heavier chalcogenides. Trimeric structures are quite rare for lithium salts of most ligands and, in the case of the chalcogenides, are currently limited to the three structures named in the Introduction. The average Li–Se bond length in **2**, *ca.* 2.47 Å, is considerably shorter than the Li–Se distance (2.57 Å) in the monomer $Li(THF)_3SeMes^*$[10,11] and those in the dimer $Li(DME)SeSi(SiMe_3)_3]_2$[12] (2.57, 2.61 Å). It is also much shorter than the Li–Se distances (2.60, 2.70 Å) in the species $[(THF)_2Li(PhSe)_2Lu(\eta^5\text{-}C_5H_5)_2]$.[30] Although longer Li–Se distances are understandable in the latter two species (owing to the higher coordination of the Li^+ ion), it is difficult to account for the large difference between **1** and $Li(THF)_3SeMes^*$. In this compound, the Li^+ ion is also four-coordinate but the –SeMes* is terminally bonded. The seleniums in **2** all have pyramidal coordination, and this phenomenon has also been observed in bridging thiolate derivatives.[31] It contrasts markedly with the structures of lithium alkoxides and aryloxides in which the bridging oxygens invariably have planar coordination. As in the structure of **1**, it may be that the large inversion barrier in pyramidally coordinated selenium (combined with a more covalent interaction with the lithiums) is sufficient to effect the observed pyramidal coordination at the seleniums.

The partial removal or deficiency of the donor molecules to give a more highly aggregated lithium salt has been observed in only a few other instances. Significantly, perhaps, these salts (obtained as in eqs 1[32,33] and 2[34]) are also lithium derivatives of

$$Li(THF)_3PHMes^{32} \xrightarrow{-THF} (1/n)[Li(THF)_2PHMes]_n^{33} \quad (1)$$

$$2[Li(THF)_2P(SiMe_3)_2]_2^{34} \xrightarrow{-2THF} [(LiP\{(SiMe_3)_2\}_2)_4(THF)_2]^{34} \quad (2)$$

the heavier main group elements. One explanation for the apparent difference between the lighter and heavier element lithium salts may involve the larger size of the heavier elements and weaker Li–element bond which permit the crystallization of the most highly solvated species in the first instance. In the case of the lighter element derivatives the stronger lithium–element (e.g. Li-N or Li-O) interactions do not allow as high degree of solvation since a greater amount of the coordination sphere is occupied by the strong Li–element interactions.

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Supplementary Material Available: Full tables of data collection parameters, atom coordinates, bond distances and angles, and hydrogen coordinates (25 pages). Ordering information is given on any current masthead page.

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