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Articles

Coordination Complexes of Zinc with Reactive $ESiMe_3$ (E = S, Se, Te) Ligands

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The complexes (*N,N′*-tmeda)$Zn(ESiMe_3)_2$ (E = S, **1a**; E = Se, **2a**; E = Te, **3a**) and (3,5-Me_2-$C_5H_3N)_2Zn(ESiMe_3)_2$ (E = S, **1b**; E = Se, **2b**; E = Te, **3b**) have been prepared in high yield by the reaction of $E(SiMe_3)_2$ with (*N,N′*-tmeda)$Zn(OAc)_2$ (**4a**) and (3,5-Me_2-$C_5H_3N)_2$-$Zn(OAc)_2$ (**4b**), respectively. Complexes **1**−**3** have been characterized spectroscopically and by means of single-crystal X-ray diffraction. All six complexes exist in the solid state as monomeric species with terminally bonded trimethylsilylchalcogenolate moieties and a distorted tetrahedral geometry of the zinc center.

Introduction

The demonstrated utility of chalcogen complexes bonded to a trimethylsilyl functionality ($RESiMe_3$, $E(SiMe_3)_2$; E = S, Se, Te, R = alkyl, aryl, ferrocenyl) in the formation of metal−chalcogen (M−E) materials has led to the preparation of monodisperse nanoparticles[1] and structurally characterized clusters[2] and nanoclusters.[3,4] Typically, the silylated chalcogen source can be reacted with a variety of metal salts[5] to yield M−E bonds via the favorable formation of a silane byproduct. The strong preference of the polarizable chalcogen elements to adopt bridging coordination modes thus leads to the "controlled" assembly of polynuclear metal−chalcogen frameworks, on both the molecular and nanoscale. This approach has recently been employed in the synthesis of a number of group 12 metal−chalcogenide/chalcogenolate clusters via the reaction of metal halide salts with the reagents $E(SiMe_3)_2$ and/or $RESiMe_3$ (E = S, Se, Te; R = alkyl or aryl) in the presence of solublizing phosphine ligands[6] accompanied by an in-depth investigation of their photophysical properties as they relate to the effects of quantum confinement.[7]

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Coordination complexes of group 12 metals containing $-ESiMe_3$ fragments represent logical routes into ternary 12−12′−16 (MM′E) materials, by exploiting the preformed M−E bond and the demonstrated reactivity of the pendant $-SiMe_3$ groups toward metal salts (M′). Typically, access to low-nuclearity group 12 metal−chalcogenolate complexes is complicated however by the tendency of these molecules to form polymeric structures or infinite lattices with bridging interactions of the chalcogenolate ligands favored over terminal coordination to the metal center.[8−11] Successful strategies to overcome these tendencies include increasing the steric bulk of the chalcogenolate ligand[12−15] and/or by the use of strongly coordinating or chelating donor ligands[16−18] to produce low-nuclearity metal chalcogenolate (M−ER) complexes (M = Zn, Cd, Hg; E = S, Se, Te) with coordination geometry of the metal center ranging from two to five. The steric crowding has the consequence however of prohibiting any additional reactivity at the chalcogen center with respect to M′−E bond formation. Thus a delicate balance is required in order to isolate $M-ESiR_3$ complexes in which the pendant $-SiR_3$ groups remain reactive.[19] This approach has been implemented in the synthesis of $(R_3P)_3CuESiMe_3$ (E = S, Se, Te; R = Et, ^{n}Pr),[20] which reacts with $Hg(OAc)_2$ or $InCl_3$ to produce ternary CuHgE[21] or CuInE[22] clusters, respectively. While the number of structurally[20,23] and spectroscopically[24] characterized d-block metal−chalcogenolate complexes with pendant reactive trimethylsilyl moieties remains small, their synthesis is an attractive goal, as complexes of this type can be used as a soluble source of "ME_n" units to access ternary $M_xM'_{1-x}E_y$ materials.[19,21,22] The development of a facile route to ternary 12−12′−16 compounds using a "reactive precursor" approach will allow for a greater development of this area of chemistry, and we have recently reported that zinc trimethylsilylchalcogenolate complexes can be utilized in the synthesis of ternary ZnCdE nanoclusters.[25−27] Herein we report the synthesis and characterization of the chalcogenolate complexes (*N,N′*-tmeda)$Zn(ESiMe_3)_2$ (E = S, **1a**; E = Se, **2a**; E = Te, **3a**) and $(3,5\text{-}Me_2\text{-}C_5H_3N)_2Zn(ESiMe_3)_2$ (E = S, **1b**; E = Se, **2b**; E = Te, **3b**).

Results and Discussion

Synthesis and Structural Characterization. Despite the continued, vibrant interest in metal-based molecules of the heavier chalcogen elements, the number of studies of homologous series of group 12 $L_2M(ER)_2$ (L = two-electron ligand; E = S, Se, *and* Te) complexes

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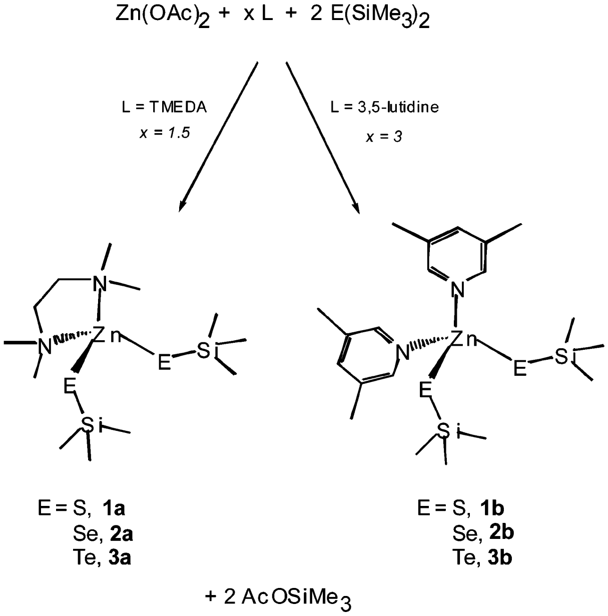
Scheme 1. Synthesis of (N,N'-tmeda)$Zn(ESiMe_3)_2$ and $(3,5\text{-}Me_2\text{-}C_5H_3N)_2Zn(ESiMe_3)_2$



is surprisingly small.[14,16,18] These molecules can be accessed by solublizing $M(ER)_2$, which are either molecular or polymeric in nature depending on the size of R, with strong donor ligands.[18] In our experience however, the direct reaction of Zn(II) salts with two or more equivalents of $E(SiMe_3)_2$ yields only insoluble and inextractable yellow solids and thus does not represent a viable route to $L_2Zn(ESiMe_3)_2$.

The well-developed coordination chemistry of Zn(II) and Cd(II) salts with strong N-donor ligands provides a facile entry into molecular complexes $L_2M(ESiMe_3)_2$. The reaction of $Zn(OAc)_2$ with an appropriate nitrogen donor ligand in tetrahydrofuran or $CHCl_3$ followed by the addition of $E(SiMe_3)_2$ at low temperatures provides a high-yield route to trimethylsilylchalcogenolate complexes of zinc(II) (Scheme 1). Metal–chalcogen bond formation occurs via the generation and elimination of $AcOSiMe_3$.

The temperature at which the addition of $E(SiMe_3)_2$ is carried out depends on the thermal stability of the final product, and the addition of at least 2 equiv of $E(SiMe_3)_2$ is vital to promote terminal coordination of the trimethylsilylchalcogenolate ligand in order to circumvent the generation of polynuclear ZnE species. The reactions are typically carried out in the presence of excess amine/imine ligand to favor the formation of monomeric complexes. This is more important in the case of **1b**–**3b**, whose monodentate 3,5-lutidine ligands are more labile than the chelating TMEDA.

The complexes can be crystallized as colorless solids from the reaction solutions by the addition of hydrocarbons and storage at low temperatures. While crystallized yields are often lowered from 100% (presumably due to limited solubility in the hydrocarbon solvent), the reactions have been shown to occur quantitatively by NMR spectroscopy. NMR scale reactions carried out in $CDCl_3$ demonstrate the complete disappearance of resonances assigned to $E(SiMe_3)_2$ and $Zn(OAc)_2$, coupled with the equivalent formation of the zinc trimethylsilylchalcogenolate complex and the anticipated side product $AcOSiMe_3$ (see Supporting Information). Complexes **1**–**3** are highly air sensitive and decompose slowly in solution if kept at elevated temperatures for extended periods. On the other hand, the complexes can be stored as solids for long periods of time without significant decomposition at −40 °C (**1**, **2**) or −80 °C (**3**) in an inert atmosphere. Complex **1a** can be stored at room temperature for extended periods in the solid state. The thermal stability of the compounds decreases in the order S > Se > Te, with TMEDA complexes generally being more stable than their 3,5-lutidine counterparts.

The monomeric structures of complexes **1**–**3** indicated by NMR spectroscopy (vide infra) were confirmed by X-ray crystallographic analyses. Crystallographic data and data collection parameters are summarized in Table 1. The N,N'-tmeda-ligated complexes **1a**, **2a**, and **3a** crystallize in the monoclinic space groups $C2/c$, $P2_1/n$ and $P2_1/c$, respectively. For the 3,5-lutidine complexes,

Table 1. Crystallographic Data and Parameters for Complexes 1–3

	1a	**2a**	**3a**	**1b**	**2b**	**3b**
radiation[a]	Mo Kα (0.71073 Å)					
	$C_{12}H_{34}N_2Si_2S_2Zn$	$C_{12}H_{34}N_2Si_2Se_2Zn$	$C_{12}H_{34}N_2Si_2Te_2Zn$	$C_{20}H_{36}N_2Si_2S_2Zn$	$C_{20}H_{36}N_2Si_2Se_2Zn$	$C_{20}H_{36}N_2Si_2Te_2Zn$
fw	392.08	485.88	583.16	490.18	583.98	681.26
T (K)	200(2)	200(2)	200(2)	200(2)	200(2)	200(2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$C2/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	25.082 (5)	8.4454(2)	8.2987(2)	9.9388(2)	9.1381(8)	9.301(2)
b (Å)	14.3889(2)	14.3403(4)	14.8275(3)	17.7413(4)	9.9833(9)	10.215(2)
c (Å)	18.7925(3)	18.7691(5)	20.5498(4)	15.1322(3)	16.591(2)	16.614(3)
α (deg)	90	90	90	90	95.712(4)	94.94(3)
β (deg)	105.055(1)	90.112(1)	110.960(1)	94.876(1)	91.288(3)	91.20(3)
γ (deg)	90	90	90	90	116.026(8)	115.66(3)
V (Å^3)	6549.5(2)	2273.1(1)	2361.3(1)	2658.56(11)	1349.7(2)	1414.5(5)
Z	12	4	4	4	2	2
ρ_{calc} (g cm^{-3})	1.189	1.420	1.640	1.225	1.437	1.602
μ (mm^{-1})	1.418	4.381	3.557	1.179	3.703	2.982
reflns coll	12 561	14 907	9608	10 340	5398	9223
ind reflns	6426 [R(int) = 0.0358]	5229 [R(int) = 0.0900]	5405 [R(int) = 0.0448]	6092 [R(int) = 0.0495]	4433 [R(int) = 0.0431]	6464 [R(int) = 0.0451]
R indices[b]	$R_1 = 0.0442$ $wR_2 = 0.1019$	$R_1 = 0.0447$ $wR_2 = 0.0808$	$R_1 = 0.0337$ $wR_2 = 0.0606$	$R_1 = 0.0455$ $wR_2 = 0.0928$	$R_1 = 0.0728$ $wR_2 = 0.1703$	$R_1 = 0.0659$ $wR_2 = 0.1604$
GOF[c]	1.008	1.003	1.012	1.012	1.109	1.054

[a] Graphite monochromator. [b] $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[wF_o^2]^2\}^{1/2}$. [c] Goodness-of-fit $= [\Sigma[w(F_o^2 - F_c^2)^2]/(N_{\text{observns}} - N_{\text{params}})]^{1/2}$ (all data).

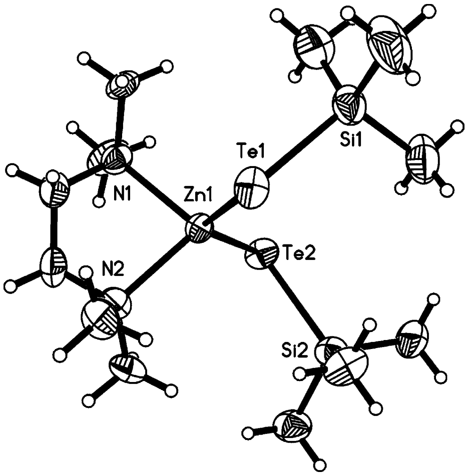


Figure 1. Molecular structure of (*N,N′*-tmeda)Zn(TeSiMe$_3$)$_2$, **3a**. Thermal ellipsoids are drawn at the 50% probability level. The crystallographic disorder of the tmeda ligand is not depicted (see Supporting Information Figure S12).

1b was solved and refined in the space group $P2/n$, while **2b** and **3b** crystallize in the triclinic space group $P\bar{1}$. The prevalent structural feature among all six complexes is the presence of terminally coordinated trimethylsilylchalcogenolate ligands, as demonstrated by the molecular structure of the tellurolate derivative **3a** presented in Figure 1. The isolation of these complexes, particularly those of the heavier congeners selenium and tellurium, is quite notable considering the inherent reactivity of these ligands and that access to monomeric group 12 complexes typically requires the use of sterically bulky chalcogenolate ligands.[12−15] The synthesis of these trimethylsilylchalcogenolates is however crucial to the development of a molecular precursor route to ternary nanomaterials, as it has been demonstrated that the introduction of bulkier constituents about the chalcogen (cf. $-$SSiMe$_2{}^t$Bu)[19e] severely affects the reactivity of the silylchalcogenolate toward other metal salts. The $-$SiMe$_3$ groups in **1**−**3** are directed away from each other in all instances in order to minimize steric repulsion between them. In complexes **1a**−**3a** the TMEDA ligand coordinates in a bidentate manner to the zinc center. The anticipated 2-fold symmetry of these complexes is not translated to the solid-state structure of **2a** and **3a** due to slight deviations in the trimethylsilyl moieties. The crystal structure of **1a** consists of two chemically equivalent but crystallographically independent molecules. In only one of these, the zinc atom lies on a 2-fold rotation axis that bisects the N−Zn−N and S−Zn−S angles. Differences between the two independent units exist primarily in the relative positions of the carbon atoms of the trimethylsilyl groups. Complexes **1b**−**3b** exist in the solid state as four-coordinate species with two monodentate 3,5-lutidine ligands. The 3,5-lutidine ligands of **1b** are twisted only slightly relative to one another with a twist angle of 9.9° between them. This twist angle is considerably larger for complexes **2b** (41.3°) (Figure 2) and **3b** (41.0°), which may be a consequence of the larger N−Zn−N angle in these complexes relative to that in **1b**.

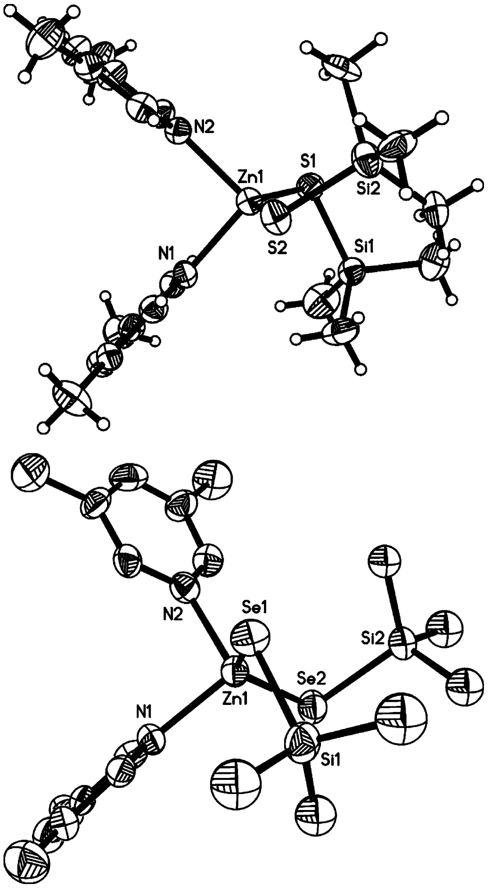


Figure 2. Perspective views of the molecular structures of (3,5-Me$_2$-C$_5$H$_3$N)$_2$Zn(SSiMe$_3$)$_2$, **1b** and (3,5-Me$_2$-C$_5$H$_3$N)$_2$-Zn(SeSiMe$_3$)$_2$, **2b** (hydrogen atoms omitted) highlighting the differences in the twist angles of the 3,5-lutidine ligands. Thermal ellipsoids are drawn at the 50% probability level. The crystallographic disorder of the $-$SiMe$_3$ groups is not depicted (see Supporting Information Figures S9 and S11).

Selected bond lengths and angles for complexes **1**−**3** are summarized in Table 2. The coordination geometry of the zinc centers in these complexes is distorted considerably from the expected tetrahedral by compression of the N−Zn−N angle. The acute angles observed in the *N,N′*-tmeda ligated complexes **1a**−**3a** are consistent with those reported for the complexes (*N,N′*-tmeda)M(EPh)$_2$ (E = S, Se, Te).[16,18] The corresponding 3,5-lutidine complexes (**1b**−**3b**) feature larger (slightly obtuse) ∠N−Zn−N. In all six complexes these constricted angles are compensated by large ∠E−Zn−E. Structural comparisons of three- and four-coordinate Zn(ER)$_2$(L)$_n$ (n = 1, 2) complexes by Bochmann and coworkers have revealed that electronic rather than steric arguments more adequately account for structures observed and that there exists a strong relationship between the identity of the L donor atom and the magnitude of the angle E−Zn−E.[14a] In general, with increasing Zn−L bond distance (decreasing s-character of the interaction between Zn and L donor atom), a consequent increase in the ∠E−Zn−E is observed.

The large E−Zn−E angles in **1**−**3** are consistent with this description and also with the angles observed in other zinc chalcogenolate complexes with amine/imine donor ligands.[13,14a,16,18] Furthermore, the significantly larger E−Zn−E angles in **1a**−**3a** versus those in the complexes (*N,N′*-tmeda)Zn(EAr)$_2$ (E = S, Se, Te)[16,18] coincide with longer Zn−N bond distances observed in

Table 2. Selected Intramolecular Bond Distances (Å) and Angles (deg) for Complexes 1−3

	1a	**1b**	**2a**	**2b**	**3a**	**3b**
Zn−E1	2.262(1)	2.272(1)	2.388(1)	2.398(2)	2.573(1)	2.582(2)
Zn−E2	2.271(1)	2.274(1)	2.379(1)	2.394(2)	2.572(1)	2.580(2)
Zn−N1	2.142(3)	2.100(2)	2.148(4)	2.105(10)	2.173(3)	2.094(7)
Zn−N2	2.163(3)	2.105(2)	2.154(3)	2.097(10)	2.166(4)	2.100(7)
Si1−E1	2.110(2)	2.114(1)	2.255(2)	2.258(4)	2.483(2)	2.485(3)
Si2−E2	2.119(2)	2.098(2)	2.255(2)	2.269(4)	2.485(2)	2.486(3)
E1−Zn−E2	129.20(4)	130.56(4)	129.21(3)	131.33(7)	128.99(2)	128.67(4)
N1−Zn−N2	85.28(12)	92.53(9)	85.12(13)	95.7(4)	84.85(13)	96.2(3)
E1−Zn−N1	111.88(9)	108.50(7)	111.40(9)	109.4(3)	109.36(8)	111.7(2)
E2−Zn−N2	109.62(8)	108.73(7)	110.72(9)	106.8(3)	106.95(9)	107.8(2)
Si1−E1−Zn	107.21(5)	104.38(4)	105.02(4)	104.3(1)	99.53(3)	101.92(7)
Si2−E2−Zn	103.41(5)	102.31(4)	101.05(4)	100.1(1)	101.09(3)	97.45(7)

Table 3. Summary of NMR Spectroscopic Data for Complexes 1−3[a]

	^{1}H (−SiMe$_3$)	^{13}C (−SiMe$_3$)	^{29}Si	^{77}Se{^{1}H}	^{125}Te{^{1}H}
1a	0.31	5.86	11.8		
2a	0.40	6.19	7.5	−514	
3a	0.54	6.73	−11.5		−1471
1b	0.15	5.39	11.8		
2b	0.23	5.74	7.9	−534	
3b	0.40	6.31	−11.4		−1234

[a] Chemical shift data reported in ppm. Spectra obtained in $CDCl_3$ (**1**, **2**) or CD_2Cl_2 (**3**) solvent.

the former. The N−Zn−N angle and Zn−N bond lengths of **1b**−**3b** are closely related to those observed for $[Zn(Te\text{-}2,4,6\text{-}Me_3\text{-}C_6H_2)_2(C_5H_5N)_2]$;[28] however the ∠N−Zn−N [96.2(3)°] and ∠Te−Zn−Te [128.67(4)°] of **3b** deviate slightly from those of the more related complex $Zn[TeSi(SiMe_3)_3]_2(C_5H_5N)_2$.[13] Thus the steric requirements of the relevant chalcogenolate ligand cannot be neglected. The Zn−E bond distances are comparable to those observed in other four-coordinate zinc complexes with terminal −ER ligands,[29] while Si−E bonds are somewhat longer than those reported for the copper complexes $(PR_3)_3Cu(ESiMe_3)$ (E = S, Se, Te).[20] This is presumably the consequence of the stronger M−E interactions (shorter M−E contacts) in **1**−**3** in comparison to those in $(PR_3)_3Cu(ESiMe_3)$. As expected, both Zn−E and Si−E bond distances increase in the order S < Se < Te.

NMR Spectroscopy. All complexes reported herein were characterized by NMR spectroscopy, and chemical shift data obtained at low temperature in $CDCl_3$ or CD_2Cl_2 are summarized in Table 3. In the ^{1}H NMR spectra of complexes **1a**−**3a** the methyl and methylene resonances of the TMEDA ligand are shifted downfield with respect to those of the free amine, verifying that TMEDA is coordinated to the metal center in solution. Similarly, the peaks assigned to the aromatic protons of the 3,5-lutidine ligands in **1b**−**3b** occur downfield of those of the free species. The chemical shifts of the protons and carbons of the trimethylsilyl unit move to lower field with increasing atomic mass of the chalcogen center, while silicon resonances move in the opposite direction, consistent with the trends observed for $(PR_3)_3Cu(ESiMe_3)$.[20]

The assignments of the spectra of **1**−**3** to monomeric species with terminally bonded $-ESiMe_3$ groups are based on the integrated ratio of the $M-ESiMe_3$ peak to those of the coordinated N-donor ligand in the ^{1}H NMR spectra. This also confirms that complexes **1b**−**3b** remain four-coordinate in solution, consistent with the structures observed in the solid state. Additionally, the ^{77}Se NMR spectra of **2a** and **2b** feature a single resonance at −514 and −534 ppm, respectively. The ^{125}Te NMR spectra of complexes **3a** and **3b** display single peaks with chemical shifts centered at −1471 and −1234 ppm, respectively. The ^{77}Se and ^{125}Te chemical shift data provide evidence for terminally bonded $-ESiMe_3$ groups in solution, as these are similar to those for $(PR_3)_3Cu(ESiMe_3)$.[20] Furthermore, the ^{125}Te chemical shifts of −1215 and −1469 ppm reported by Bonasia and Arnold[13] for the terminal sitel ligands of $\{Zn[TeSi(SiMe_3)_3]_2\}_2$ and $Zn[TeSi(SiMe_3)_3]_2(C_5H_5N)_2$, respectively, are similar to those observed for **3a** and **3b**. In contrast, the resonance assigned to the bridging sitel ligands in $\{Zn[TeSi(SiMe_3)_3]_2\}_2$ was significantly shifted upfield to −783 ppm. No coupling to ^{29}Si was resolved in the ^{77}Se or ^{125}Te NMR spectra of the complexes reported here.

Ultraviolet Spectroscopy. The solution electronic absorption spectra of complexes **1a** and **1b** show a broad absorption band at 259 and 255 nm, respectively (Figure 3a). A shoulder at 268 nm in the spectrum of **1b** can be attributed to a $\pi-\pi^*$ transition of the coordinated 3,5-lutidine ligands,[30] as a band at similar energy is also observed in the spectrum of $(3,5\text{-}Me_2\text{-}C_5H_3N)_2Zn(OAc)_2$ (**4b**). Given that the UV−visible spectrum of (*N,N′*-tmeda)$Zn(OAc)_2$ (**4a**) displays no discernible maximum below 200 nm, absorptions from the coordinated amine ligands of **1a** are also not expected in this region. It has been reported that the energy of the 4s orbital of the Zn(II) center in the mononuclear zinc thiolate complexes $[Zn(SR)_4]^{2-}$ (R = Ph,[31] 2-Ph-C_6H_4)[32] is too high to accommodate a $S(3p) \rightarrow Zn(4s)$ ligand-to-metal charge transfer (LMCT) transition. In these and related complexes[33] absorption bands to lower energy of 200 nm have been designated as intraligand (IL) transitions of the arylthiolate ligands. An assignment of the bands in the spectra of **1a**,**1b** to IL $[S(3p) \rightarrow Si(3d)]$ transitions of the trimethylsilylthiolate ligands is not reasonable given that the free anion $[Me_3SiS^-]$[34] and $S(SiMe_3)_2$[35] absorb at higher energy. Furthermore, investigations of the absorption spectra of TCE·R−S−R′ (TCE =

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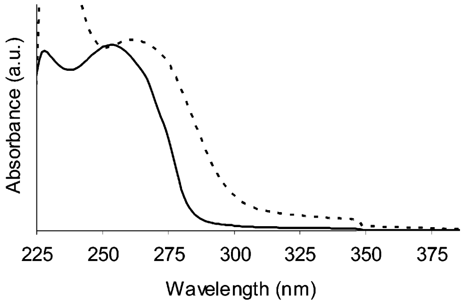

Figure 3. Absorption spectra of (*N,N′*-tmeda)Zn(SSiMe$_3$)$_2$ (**1a**) (- - -) and (3,5-Me$_2$-C$_5$H$_3$N)$_2$Zn(SSiMe$_3$)$_2$ (**1b**) (—) in dichloromethane.

tetracyanoethylene, R, R′ = ^{n}Bu, ^{i}Pr, SiMe$_3$) charge transfer complexes demonstrated a shift to higher energy for R = −SiMe$_3$, which was attributed to a lowering of the energy of the S(3p) orbital due to the presence of silicon.[36] The broad bands in the region 250−260 nm in the spectra of **1a** and **1b** are therefore assigned to S(3p) → Zn(4s) LMCT transitions. The evident differences in the HOMO−LUMO gap of **1a** and **1b** versus [Zn(SR)$_4$]$^{2-}$ can be interpreted as a consequence of the anionic nature of the latter, resulting in a relative increase in energy of the Zn 4s orbital. Indeed, evidence for the involvement of the metal-based LUMO in electronic transitions in related neutral complexes has been presented: the photophysical properties of Zn(II) complexes with π-donor thiolate ligands and good π-acceptor N-heterocyclic ligands such as bipyridine and phenanthroline have been rationalized by Koester[37] and Crosby[38] in terms of an interligand trans-metallic charge transfer (ITCT) from the HOMO of the thiolate across the metal to the LUMO of the acceptor ligand. Similar transitions could be possible for **1b**; however the π* orbitals of the 3,5-lutidine ligands occur at higher energy with respect to the more conjugated ligands, and the spectrum does not support such an assignment.

The absorption spectra of the trimethylsilylselenolate complexes **2a** and **2b** are presented in Figure 4. Consistent with the assignment of the spectra of **1a** and **1b**, the broad maxima at 292 nm (**2a**) and 297 nm (**2b**) are attributed to Se(4p) → Zn(4s) LMCT transitions. This is substantiated by the presence of a peak at similar energy in the absorption spectrum of (*N,N′*-tmeda)Zn(SePh)$_2$.[39] Interestingly, the LMCT transition of **2b** is observed at slightly longer wavelength than that of the *N,N′*-tmeda analogue, which is contrary to the effects observed for the thiolate complexes. The explicit source of this discrepancy is not clear at this point. The spectrum of complex **2b** also exhibits the $\pi-\pi^*$ transition of the 3,5-lutidine ligands at 268 nm. An additional peak (**2a**, 237 nm; **2b**, 235 nm) lying energetically between those observed for [Me$_3$SiSe$^-$][34] and Se(SiMe$_3$)$_2$ (220 nm) is assigned to intraligand [Se(4p) → Si(3d)] transitions of the trimethylsilylselenolate ligands.

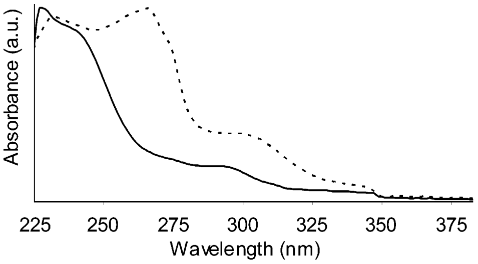

Figure 4. Absorption spectra of (*N,N′*-tmeda)Zn(SeSiMe$_3$)$_2$ (**2a**) (- - -) and (3,5-Me$_2$-C$_5$H$_3$N)$_2$Zn(SeSiMe$_3$)$_2$ (**2b**) (—) in dichloromethane.

Conclusions

The complexes reported herein represent the first examples of zinc(II) compounds with trimethylsilylchalcogenolate ligands. Crystallographic and spectroscopic analysis revealed that these complexes are monomeric both in solution and in the solid state. The molecules exhibit terminally coordinated, reactive trimethylsilylchalcogenolate ligands and yet can be stored under inert atmosphere for extended periods. These complexes are convenient precursors for the generation of ternary MM′E nanocluster complexes.[25−27]

Experimental Section

Syntheses. All synthetic and handling procedures were carried out under an atmosphere of high-purity dried nitrogen using standard double-manifold Schlenk line techniques and gloveboxes. Nonchlorinated solvents were dried and collected using an MBraun MB-SP Series solvent purification system with tandem activated alumina (tetrahydrofuran) or activated alumina/activated copper redox catalyst (pentane, toluene).[40] Chloroform, chloroform-*d*, and dichloromethane were dried and distilled over P$_2$O$_5$, while tetramethylethylenediamine (TMEDA) and 3,5-lutidine were distilled over calcium hydride and sodium, respectively. Zinc acetate was purchased from Aldrich in 99.999% purity and used as supplied. Cadmium acetate was purchased as the dihydrate and dried in vacuo at 135 °C for 12 h. The reagents E(SiMe$_3$)$_2$ (E = S, Se, Te) were synthesized according to literature procedures.[27,41] Chemical analyses were prohibited by the inherent chemical reactivity and considerable susceptibility of the trimethylsilylchalcogenolate ligands of complexes **1**−**3** to hydrolysis and oxidation upon even very brief exposure to air. Sample homogeneity and purity were confirmed by NMR spectroscopy (see Supporting Information).

(*N,N′*-tmeda)Zn(SSiMe$_3$)$_2$, 1a. Zinc acetate (0.512 g, 2.79 mmol) was dissolved in 65 mL of THF by the addition of TMEDA (0.63 mL, 4.19 mmol). S(SiMe$_3$)$_2$ (1.17 mL, 5.58 mmol) was added at room temperature, and the resulting clear, colorless solution was stirred for 30 min. Removal of THF in

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(34) LiSSiMe$_3$ and LiSeSiMe$_3$ were prepared by the reported method: Segi, M.; Kato, M.; Nakagima, T.; Suga, S.; Sonoda, N. *Chem. Lett.* **1989**, 1009−1012. UV−visible spectra [$\lambda_{\max}$ = 239 nm (S), 245 nm (Se)] in THF solution were obtained immediately following their preparation.

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(39) *N,N′*-tmeda)Zn(SePh)$_2$ was prepared by the addition of TMEDA and PhSeSiMe$_3$ to Zn(OAc)$_2$ at 0 °C in THF. The solvent was removed in vacuo, and the product was washed and dried. The identity of the complex was confirmed by NMR spectroscopy as reported in ref 18a.

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vacuo and washing with pentane produced pure **1a** as a white solid. The complex can be crystallized from a 3:1 hexane/THF mixture by storing the solution at −80 °C, under which conditions colorless, rodlike crystals suitable for X-ray analysis form after 2 days. Yield: 1.03 g (94%). Mp: 134−135 °C (dec). ^{1}H NMR (CDCl$_3$, 223 K, δ): 2.62 (s, br, N−CH$_2$), 2.51 (s, br, N−CH$_3$), 0.31 (s, SiMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 223 K, δ): 56.48 (s, N−CH$_2$), 47.85 (s, N−CH$_3$), 5.86 (s, SiMe$_3$). ^{29}Si NMR (CDCl$_3$, 223 K, δ): 11.8 ppm.

***N,N′*-tmeda)Zn(SeSiMe$_3$)$_2$, 2a.** The preparation was carried out in an analogous manner to **1a**, with zinc acetate (0.493 g, 2.68 mmol) and TMEDA (0.61 mL, 4.03 mmol), except that Se(SiMe$_3$)$_2$ (1.16 mL, 5.37 mmol) was added at 0 °C and stirred for 15 min at that temperature. Pure **2a** could be isolated as a white powder by removal of the solvent in vacuo, followed by washing with pentane and drying for 2 h at 0 °C. Single, X-ray quality crystals of this complex were obtained in the same manner as for **1a**. Yield: 1.20 g (92%). Mp: 62−65 °C (dec). ^{1}H NMR (CDCl$_3$, 223 K, δ): 2.60 (s, br, N−CH$_2$), 2.51 (s, br, N−CH$_3$), 0.40 (s, SiMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 223 K, δ): 56.40 (s, N−CH$_2$), 48.32 (s, N−CH$_3$), 6.19 (s, SiMe$_3$). ^{29}Si NMR (CDCl$_3$, 223 K, δ): 7.5. ^{77}Se{^{1}H} NMR (CDCl$_3$, 223 K, δ): −514 ppm.

(*N,N′*-tmeda)Zn(TeSiMe$_3$)$_2$, 3a. A solution of zinc acetate (0.225 g, 1.23 mmol) and TMEDA (0.28 mL, 1.84 mmol) in CH$_2$Cl$_2$ (6 mL) was treated with freshly prepared Te(SiMe$_3$)$_2$ at −78 °C, resulting in a pale yellow solution. Removal of ∼80% of the solvent in vacuo at low temperature, followed by the addition of cold (−78 °C) pentane (50 mL), yielded a white precipitate. The mother liquor was decanted off and the solid was washed with cold pentane. Upon warming slightly while drying in vacuo, the surface of the crystalline solid developed a pale orange color; however the sample remained spectroscopically pure. Complex **3a** was crystallized from the reaction solution (in CH$_2$Cl$_2$) by the addition of cold heptane to the point of incipient precipitation and storage at −80 °C for 3 days. Yield: 0.510 g (71%). Mp: 5 °C (dec). ^{1}H NMR (CDCl$_3$, 213 K, δ): 2.61 (s, br, CH$_2$), 2.53 (s, br, CH$_3$), 0.54 (s, SiMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 213 K, δ): 57.11 (s, CH$_2$), 49.40 (s, CH$_3$), 6.73 (s, SiMe$_3$). ^{29}Si NMR (CDCl$_3$, 213 K, δ): −11.5. ^{125}Te{^{1}H} NMR (CDCl$_3$, 213 K, δ): −1471 ppm.

(3,5-Me$_2$-C$_5$H$_3$N)$_2$Zn(SSiMe$_3$)$_2$, 1b. Zinc acetate (0.40 g, 2.18 mmol) was dissolved in 6 mL of CHCl$_3$ with 3,5-lutidine (0.74 mL, 6.54 mmol). The CHCl$_3$ was removed in vacuo and replaced with THF (8 mL), and after cooling to 0 °C, the solution was treated with S(SiMe$_3$)$_2$ (0.91 mL, 4.36 mmol) and stirred for 15 min. at that temperature. The THF was removed in vacuo, and the resulting white solid of pure **1b** was washed several times with pentane to remove excess 3,5-lutidine. The complex was recrystallized from a mixture of CHCl$_3$ (8 mL) and pentane (150 mL) to produce single blocklike crystals suitable for X-ray crystallography by cooling to −80 °C for 2 days. Yield: 0.98 g (90%). Mp: 89−92 °C (dec). ^{1}H NMR (CDCl$_3$, 223 K, δ): 8.41 (s, br, *ortho*-H, aryl), 7.44, (s, br, *para*-H, aryl), 2.23 (s, br, *meta*-CH$_3$), 0.15 (s, −SiMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 223 K, δ): 145.45 (s, *ortho*-C, aryl), 140.63 (s, *meta*-C, aryl) 134.31 (s, *para*-C, aryl), 18.23 (s, *meta*-CH$_3$), 5.39 (s, SiMe$_3$). ^{29}Si NMR (CDCl$_3$, 223 K, δ): 11.8 ppm.

(3,5-Me$_2$-C$_5$H$_3$N)$_2$Zn(SeSiMe$_3$)$_2$, 2b. The complex was prepared as for complex **1b** using zinc acetate (0.410 g, 2.23 mmol) and 3,5-lutidine (0.76 mL, 6.70 mmol) except that Se(SiMe$_3$)$_2$ (0.97 mL, 4.46 mmol) was added at −78 °C and then the reaction was warmed slowly until a clear, colorless solution was obtained. Complex **2b** was isolated as a white solid by removal of ∼90% of the THF in vacuo at 0 °C, followed by precipitation with cold pentane. The solid was washed with pentane and dried under vacuum (0 °C) for 30 min. Single crystals of **2a** suitable for X-ray analysis were obtained in the same manner as **1b**. Yield: 1.12 g (86%). Mp: 53−55 °C (dec). ^{1}H NMR (CDCl$_3$, 223 K, δ): 8.44 (s, br, *ortho*-H, aryl), 7.44, (s, br, *para*-H, aryl), 2.25 (s, br, *meta*-CH$_3$), 0.23 (s, −SiMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 223 K, δ): 8.44 (s, br, *ortho*-H, aryl), 7.44, (s, br, *para*-H, aryl), 2.25 (s, br, *meta*-CH$_3$), 0.23 (s, −SiMe$_3$). ^{13}C{H} NMR (CDCl$_3$, 223 K, δ): 145.65 (s, *ortho*-C, aryl), 140.60 (s, *meta*-C, aryl) 134.29 (s, *para*-C, aryl), 18.28 (s, *meta*-CH$_3$), 5.74 (s, SiMe$_3$). ^{29}Si NMR (CDCl$_3$, 223 K, δ): 7.9. ^{77}Se{^{1}H} NMR (CDCl$_3$, 223 K, δ): −534 ppm.

(3,5-Me$_2$-C$_5$H$_3$N)$_2$Zn(TeSiMe$_3$)$_2$, 3b. To a solution of zinc acetate (0.210 g, 1.14 mmol) and 3,5-lutidine (0.39 mL, 3.43 mmol) in CH$_2$Cl$_2$ (3 mL) was added freshly distilled Te(SiMe$_3$)$_2$ at −70 °C. The addition of cold (−70 °C) pentane (80 mL) yielded a white precipitate. The mother liquor was decanted off, and the solid was washed with cold pentane. Like **3a**, the surface of the crystalline solid developed a pale orange color while drying in vacuo, but the solid remained pure **3b** as determined by NMR spectroscopy. Alternatively, addition of cold (−78 °C) pentane to the reaction solution to the point of incipient precipitation, followed by storage of the reaction mixture at −80 °C for 3 days, resulted in the formation of colorless crystals amidst a small amount of amorphous brown precipitate. Yield: 0.46 g (69%). Mp: −10 °C (dec). ^{1}H NMR (CD$_2$Cl$_2$, 223 K, δ): 8.45 (s, br, *ortho*-H, aryl), 7.47, (s, br, *para*-H, aryl), 2.26 (s, br, *meta*-CH$_3$), 0.40 (s, −SiMe$_3$). ^{13}C{H} NMR (CD$_2$Cl$_2$, 223 K, δ): 145.45 (s, *ortho*-C, aryl), 140.63 (s, *meta*-C, aryl) 134.31 (s, *para*-C, aryl), 18.23 (s, *meta*-CH$_3$), 6.31 (s, SiMe$_3$). ^{29}Si NMR (CD$_2$Cl$_2$, 223 K, δ): −11.4. ^{125}Te{^{1}H} NMR (CD$_2$Cl$_2$, 223 K, δ): −1234 ppm.

(*N,N′*-tmeda)Zn(OAc)$_2$, 4a. Zinc acetate (0.24 g, 1.31 mmol) was dissolved in CHCl$_3$ (5 mL) by the addition of TMEDA (0.20 mL, 1.31 mmol). The solution was evaporated to dryness, yielding colorless crystals. The crystalline solid was confirmed to be pure **4a** by comparison of crystallographically determined cell constants to those reported.[42] Yield: 0.15 g (94%). IR (CHCl$_3$): 2956(s), 2923(vs) 2856(vs), 1602(s), 1592(s), 1522(s), 1482(s), 1424(s), 1392(s), 1344(w), 1280(sh,w), 1223(vs), 1146(w), 1047(m), 1039(m), 941(w), 929(s), 895(w), 856(m), 679(vs), 627(m), 489(w). ^{1}H NMR (CDCl$_3$, 293 K, δ): 2.56 (s, br, N−CH$_2$), 2.38 (s, br, N−CH$_3$), 1.93 (s, acetato, CH$_3$). ^{13}C{H} NMR (CDCl$_3$, 293 K, δ): 179.89 (s, carbonyl), 55.88 (s, N−CH$_2$), 45.36 (s, N−CH$_3$), 20.77 (s, acetato CH$_3$).

(3,5-Me$_2$-C$_5$H$_3$N)$_2$Zn(OAc)$_2$, 4b. 3,5-Lutidine (0.37 mL, 3.27 mmol) was added to a suspension of zinc acetate (0.30 g, 1.63 mmol) in CH$_2$Cl$_2$ (10 mL), producing a clear colorless solution. The solvent was removed in vacuo, and the resulting white solid was washed with pentane and dried. Yield: 0.60 g (93%). Anal. Calcd: C, 54.39; H, 6.08, Found: C, 54.49; H, 6.44. IR (CHCl$_3$): 3070(sh,m), 3020(vs), 2979(sh,vs), 2929(m), 2871(w), 1608(vs), 1591(vs), 1525(s), 1470(sh,s), 1430(vs), 1393(vs), 1336(s), 1283(sh,m), 1248(sh,vs), 1223(vs), 1178(s), 1152(s), 1048(m), 1038(m), 1017(m), 929(m), 865(m), 850(w), 702(vs), 667(vs), 620(m), 539(w), 499(w). ^{1}H NMR (CDCl$_3$, 223 K, δ): 8.35 (s, *ortho*-H, aryl), 7.44, (s, *para*-H, aryl), 2.30 (s, *meta*-CH$_3$), 2.07 (s, −OC(O)CH$_3$). ^{13}C{H} NMR (CDCl$_3$, 223 K, δ): 179.42 (s, acetato-CO), 146.70 (s, *ortho*-C, aryl), 139.73 (s, *meta*-C, aryl) 133.95 (s, *para*-C, aryl), 22.84 (s, acetato-CH$_3$), 18.51 (s, *meta*-CH$_3$) ppm.

X-ray Crystallography and Structure Solution. X-ray diffraction data were obtained on single crystals of complexes **1**−**3**, which were mounted on a glass fiber after being immersed in mineral oil or cold heptane to prevent decomposition. Crystals were placed in a cold stream of nitrogen during collection. Measurements were carried out on a Nonius Kappa-CCD diffractometer with graphite-monochromated Mo Kα_1 (λ = 0.71073) radiation. Intensity data were collected using the software COLLECT (Nonius, 1998). Nonius DENZO software was used for crystal cell refinement and data reduction, while scaling was performed using Nonius SCALE-PACK. Data were corrected for Lorentz and polarization effects; however analytical absorption corrections were not applied. The structures were solved by direct methods and refined via full-matrix least-squares techniques using the SHELXTL (G. M. Sheldrick, Madison, WI) program. The weighting scheme employed was of the form $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ (a, b = refined variables, $P = {}^1/_3\max(F_o^2, 0) + {}^2/_3F_c^2$), $R_1 = \sum||F_o| - |F_c|/\sum|F_o|$ and $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2/\sum[wF_o^2]^2\}^{1/2}$. All non-hydrogen atoms in complexes **1**−**3** were refined with anisotropic thermal parameters, with the exception of carbon atoms that were refined as disordered pairs. Complete details of site disorder models are contained in the Supporting Information. The atomic coordinates of all hydrogen atoms were constrained to their calculated positions using a riding model based on the positions of their corresponding carbon atoms. Crystals of complex **2b** invariably contained a minor nonmerohedral twin component 180° about [0 1 0] in the reciprocal lattice. ROTAX software was used to determine the twin law,[43] while hklf5 was calculated using WINGX.[44] Untwinning resulted in an improvement in R_1 (11.21 to 7.28), Goof (2.054 to 1.109), and K (13.9 to 4.7) [K = Mean[F_o^2]/Mean[F_c^2]. The largest difference peak decreased from 2.27 to 0.91 e Å^{-3} for the untwinned data. The carbon atoms of the trimethylsilyl groups were refined isotropically, with those of one of the $-SiMe_3$ units being disordered over two positions with a 50:50 site occupancy.

Physical Measurements and Instrumentation. NMR spectra [^{1}H (399.763 MHz), ^{13}C{^{1}H} (100.522 MHz), ^{29}Si (79.423 MHz), ^{77}Se{^{1}H} (76.217 MHz), ^{125}Te{^{1}H} (126.033 MHz)] were recorded on a Varian Inova 400 NMR spectrometer. ^{29}Si chemical shifts were obtained indirectly from resonance magnetization transfer from the corresponding protons of the $-SiMe_3$ groups (J_{Si-H} = 6 Hz) using a gradient heteronuclear multibond coupling (gHMBC) experiment. ^{1}H and ^{13}C NMR chemical shifts were referenced internally to $SiMe_4$ using the residual proton and carbon signal of the deuterated solvent, while ^{29}Si chemical shifts were referenced externally to $SiMe_4$. ^{77}Se{^{1}H} and ^{125}Te{^{1}H}NMR spectra were referenced to the external standards Me_2Se and Me_2Te using $PhSeSiMe_3$ and $PhTeSiMe_3$ as secondary references. Ultraviolet−visible spectroscopy was performed on a Varian Cary 100 spectrometer, while infrared spectra were obtained using a Perkin-Elmer System 2000 FT-IR spectrometer.

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Supporting Information Available: Crystallographic information files (.cif) and site disorder models for complexes **1a**−**3b**, along with ^{1}H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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