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Synthesis and Characterization of New Thiolato Derivatives of Lithium, Magnesium, and Zinc: Examples of Two-Coordinate Lithium and Zinc Species Ligated by Sulfur

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The synthesis and characterization of new thiolato derivatives of lithium, magnesium, and zinc are described. Treatment of HSC_6H_3-2,6-Mes_2 in Et_2O with 1 equiv of *n*-BuLi affords the asymmetric lithium thiolate dimer $[\{LiSC_6H_3\text{-}2,6\text{-}Mes_2\}_2(Et_2O)_2]$ (**1**), in which only one of the Li^+ ions is solvated by ethers, the other being solvated by thiolates alone. The addition of 2 equiv of thiol to MgR_2 (R = *n*-Bu, *s*-Bu) produces the magnesium thiolate $Mg(SC_6H_3\text{-}2,6\text{-}Mes)_2$ (**2**), which probably has a monomeric structure in solution. Similarly, treatment of $Zn\{N(SiMe_3)_2\}_2$ in hexane with 2 equiv of the bulky thiol HSC_6H_3-2,6-Mes_2 gives a monomeric zinc thiolate $Zn(SC_6H_3\text{-}2,6\text{-}Mes_2)_2$ (**3**). Two-coordinate environments, in which a lithium in **1** and zinc in **3** are coordinated by two thiolate sulfurs, have been confirmed by X-ray analysis. Both **1** and **3** also exhibit weak metal−ligand interactions involving the ortho mesityl group(s) of the thiolate ligand. All compounds were characterized by IR and ^1H NMR spectroscopy. Crystal data with Mo Kα (λ = 0.710 73 Å) radiation at 130 K: **1**, $[\{LiSC_6H_3\text{-}2,6\text{-}Mes_2\}_2(Et_2O)_2]$, a = 10.948(2) Å, b = 16.765(3) Å, c = 28.081(6) Å, β = 97.67(3)°, monoclinic, Z = 4, space group $P2_1/c$, R = 0.063; **3**, $Zn(SC_6H_3\text{-}2,6\text{-}Mes_2)_2$, a = 16.840(5) Å, b = 14.371(3) Å, c = 18.253(6) Å, β = 114.15(2)°, monoclinic, Z = 4, space group $P2_1/c$, R = 0.050.

Introduction

Metal thiolate complexes have attracted considerable interest owing to their biological relevance and the diversity of their structures.[1−3] Nonetheless, the characterization of neutral homoleptic metal thiolates has often proved difficult owing to their tendency to form insoluble polymers through strong thiolato bridging. The formation of insoluble polymeric materials can often be prevented by synthesizing anionic species and/or by using donor solvents to reduce the degree of aggregation. The resultant compounds exist as either anionic clusters or anionic monomers, usually with a coordination number of 4 at the metal.[1−3] Recently, there has been much interest in using sterically demanding thiolates to decrease the degree of association in and add lipophilicity to these compounds.[2−12] The use of very bulky thiolate ligands such as $-SC_6H_2$-2,4,6-*t*-Bu_3 (−SMes*),[4−8] $-SC_6H_2$-2,4,6-*i*-Pr_3,[9] $-SC_6H_3\text{-}2,6\text{-}(SiMe_3)_2$,[10] $-SC_6H_2$-2,4,6-Ph_3 (−STriph),[11] and $-SC_6H_3$-2,6-Mes_2[12] has produced a number of well-characterized low-coordinate homoleptic thiolates. The effectiveness of this approach was first demonstrated over 10 years ago when a series of monomeric two-coordinate thiolate complexes $M(SMes^*)_2$ (M = Ge, Sn, Pb), in which the divalent metal also possessed a stereochemically active lone pair, were readily synthesized.[4] When the use of the SMes* ligand was applied to other metals, a dimeric structure of formula $[M(SMes^*)_2]_2$ (M = Mn,[5] Fe,[5] Co,[5] Zn,[6−8a] Cd[13]) was obtained. More recent work showed that the use of the more sterically demanding ligand $-SC_6H_3$-2,6-Mes_2 enabled the stabilization of the first two-coordinate, monomeric, transition metal thiolate species $Fe(SC_6H_3\text{-}2,6\text{-}Mes_2)_2$.[12] In this paper the use of this ligand to achieve low coordination numbers in lithium, magnesium, and zinc is now described.

Experimental Section

General Procedures. All reactions were performed under N_2 by using either modified Schlenk techniques or a Vacuum Atmospheres HE 43-2 drybox. Solvents were freshly distilled from sodium−potassium alloy and degassed twice before use. HSC_6H_3-2,6-Mes_2[12] and $Zn\{N(SiMe_3)_2\}_2$[14] were prepared by published procedures. Dibutylmagnesium (Aldrich, 1 M heptane solution) was used as received. Infrared spectra were recorded in the range 4000−200 cm^{-1} as a Nujol mull between CsI plates using a Perkin-Elmer PE-1430 spectrometer. ^1H NMR spectra were recorded on a General Electric QE-300 spectrometer.

Preparations. $[\{LiSC_6H_3\text{-}2,6\text{-}Mes_2\}_2(Et_2O)_2]$ (1). HSC_6H_3-2,6-Mes_2 (0.69 g, 2.0 mmol) dissolved in diethyl ether (40 mL) was treated dropwise with a solution of *n*-BuLi (1.3 mL of a 1.6 M solution in hexane). The reaction mixture was allowed to stir for several hours, whereupon the volume was reduced to incipient crystallization. Cooling overnight in a −20 °C freezer produced large colorless crystals of **1** in

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ca. 80% yield. Mp: 230 °C (140 °C desolvation). ^{1}H NMR: δ 0.89 (t, 6H, Et_2O), 2.03 (s, 12H, *o*-Me), 2.24 (s, 6H, *p*-Me), 3.15 (q, 4H, Et_2O), 6.78 (d, 2H, *m*-H (Ph)), 6.80 (s, 4H, *m*-H (Mes)), 6.92 (t, 1H, *p*-H). IR (cm^{-1}): 1610 s, 1572 s, 1300 w, 1280 w, 1260 w, 1238 s, 1178 m, 1155 s, 1120 s, 1075 s, 1040 s, 1030 w, 1010 m, 950 m, 930 s, 902 w, 890 w, 880 w, 850 s, 822 m, 792 s, 775 m, 740 s, 730 s, 652 w, 590 s, 570 s, 570 m, 545 m, 462 s, 407 w, 380 s, 350 m, 335 s, 280 m.

$Mg(SC_6H_3$-2,6-$Mes_2)_2$ (2). HSC_6H_3-2,6-Mes_2 (0.69 g, 2.0 mmol) was dissolved in hexane (70 mL). Dibutylmagnesium (1.0 mL of a 1.0 M solution in heptane) was added dropwise via syringe. The solution was heated briefly to reflux with a heat gun and allowed to stir for 4 h after which a white microcrystalline precipitate of **2** had formed in *ca.* 80% yield. Mp: 272–275 °C. ^{1}H NMR: δ 1.99 (s, 12H, *o*-Me), 2.22 (s, 6H, *p*-Me), 6.65 (d, 2H, *m*-H (Ph), ^4J = 7.5 Hz), 6.81 (s, 4H, *m*-H (Mes)), 6.86 (t, 1H, *p*-H, ^4J = 7.8 Hz). IR (cm^{-1}): 1610 m, 1570 m, 1300 w, 1260 w, 1245 w, 1155 w, 1112 w, 1085 w, 1042 m, 970 w, 845 s, 795 s, 740 s, 465 m, 410 m.

$Zn(SC_6H_3$-2,6-$Mes_2)_2$ (3). The thiol HSC_6H_3-2,6-Mes_2 (1.06 g, 3 mmol) dissolved in hexane (75 mL) was added dropwise to $Zn\{N(SiMe_3)\}_2$ (0.59 g, 1.5 mmol) in hexane (10 mL) with stirring. The solution was briefly heated to reflux with a heat gun and stirred for 1 h after, which a white crystalline precipitate was formed. Heating the solution caused the precipitate to redissolve. Cooling overnight produced large colorless crystals of **3** in *ca.* 80% yield. Mp: 229–231 °C. ^{1}H NMR: δ 1.97 (s, 12H, *o*-Me), 2.23 (s, 6H, *p*-Me), 6.64 (d, 2H, *m*-H (Ph), ^4J = 7.5 Hz), 6.81 (s, 4H, *m*-H (Mes)), 6.84 (t, 1H, *p*-H, ^4J = 7.8 Hz). IR (cm^{-1}): 1722 m, 1605 m, 1565 m, 1300 w, 1260 w, 1240 w, 1160 m, 1110 w, 1090 w, 1040 m, 960 w, 888 m, 847 s, 795 s, 775 m, 582 m, 568 w, 542 w, 465 s, 418 m, 380 w, 341 m, 293 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 15.

The data for both **1** and **3** were collected at 130 K with the use of a Siemens R3m/V diffractometer (Mo Kα radiation, λ = 0.710 73 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 installed on a MicroVax 3200 work station. Scattering factors were obtained from ref 16a. An absorption correction was applied by using the method described in ref 16b. Some details for the data collection and refinement are given in Table 1. Coordinates for selected atoms are given in Table 2. Important bond distances and angles are provided in Table 3. Further details are available in the supplementary material. The crystal structures of **1** and **3** were solved by direct methods and difference Fourier maps. Both crystal structures were refined by full-matrix least-squares procedures. 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 $U_H \sim 1.3U_C$ for **1** and for **3**. Two of the ethyl groups of the Et_2O units in **1** were found to be disordered. A model using variable refined occupancies and bond length restraints of the affected atoms was employed. Some atoms in structure **1** displayed large thermal motions, and four carbon atoms were restrained during refinement.

Results and Discussion

Structural Descriptions. The crystallographic data for **1** (Figure 1) show that the structure consists of asymmetric dimers with no close interactions between neighboring molecules. The core is composed of a planar Li_2S_2 array with internal angles at S(1), S(2), Li(1), and Li(2) of 77.7(2), 78.4(3), 98.3(2), and 105.2(3)°, respectively. The Li(1) center has a distorted tetrahedral geometry and is coordinated to two thiolate sulfurs and two diethyl ethers with Li(1)—S bond lengths of 2.521(7) and 2.473(7) Å. In contrast, Li(2) bridges two thiolate sulfurs and is essentially two-coordinate with a bent geometry. The Li(2)—S bond lengths are 2.366(7) and 2.382(8) Å. There are also close interactions between Li(2) and the ortho mesityl substituent carbons. The closest Li(2)—mesityl ring ring contacts involve Li(2)--C(8) (2.637 Å), Li(2)--C(7) (2.725 Å), Li(2)--C(9) (2.775 Å), and Li(2)--C(40) (2.801 Å). Other possible interactions between Li(2) and the mesityl rings are greater than 2.904 Å.

Table 1. Crystallographic Data for **1** and **3**[a]

	1	**3**
formula	$C_{56}H_{70}Li_2O_2S_2$	$C_{48}H_{50}S_2Zn$
fw	853.1	756.4
color and habit	colorless prisms	colorless prisms
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	10.948(2)	16.840(5)
b, Å	16.765(2)	14.371(3)
c, Å	28.081(6)	18.253(6)
β, deg	97.67(3)	114.15(2)
V, Å^3	5108(3)	4030(2)
Z	4	4
cryst dimens, mm^3	0.40 × 0.50 × 0.80	0.20 × 0.32 × 0.40
d_{calcd}, g cm^{-3}	1.109	1.246
μ(Mo Kα), mm^{-1}	1.43	7.45
no. of obsd rflns	5514 ($F \geq 6.0\sigma(F)$)	5149 ($F \geq 4\sigma(F)$)
R,[b] R_w[b]	0.063, 0.073	0.050, 0.064

[a] Data were collected at 130 K using a Siemens R3m/V diffractometer with monochromated Mo Kα radiation. [b] $R = \sum||F_o| - |F_c||/|F_o|$; $R_2 = \sum||V_o| - |V_c||2^{1/2}/\sum|F_o w^{1/2}|$.

$Zn(SC_6H_3$-2,6-$Mes_2)_2$ (**3**) crystallizes as discrete monomers with no close interactions between neighboring molecules, as illustrated in Figure 2. The zinc atom is coordinated by two thiolate ligands which afford nonlinear geometry (S—Zn—S) angle 151.7(1)°). The Zn—S bond lengths are 2.199(1) and 2.193(1) Å, and the Zn—S—C angles are 105.6(1) and 106.4(2)°. Possible interactions between the zinc center and various carbon atoms of the ortho mesityl substituents are also apparent. The closest zinc—mesityl ring contacts involve Zn(1)--C(31) (2.651 Å) and Zn(1)--C(7) (2.718 Å). Other possible interactions with the mesityl rings are all longer than 2.930 Å.

Discussion

Compound **1** was synthesized in a straightforward manner, and in good yield, by treatment of the thiol with *n*-BuLi. It was isolated as colorless crystals of formula $[\{LiSC_6H_3$-2,6-$Mes_2\}_2(Et_2O)_2]$. Solution ^{1}H NMR studies confirm a 1:1 thiolate:diethyl ether ratio with only one thiolate and ether environment observable on the NMR time scale at room temperature. A number of related lithium complexes of monodentate thiolate ligands have been structurally characterized. These include molecular compounds $[Li_2(THF)_{3.5}\{SC(SiMe_3)_3\}_2]$,[17] $[Li_2(THF)_4\{SCH(SiMe_3)_2\}_2]$,[17] $Li(THF)_3SMes^*$,[18] $Li(THF)_3STriph$,[11] $Li(py)_3SC_6H_5$-2-Me,[19] and the polymers $[Li(py)_2SPh]_n$[19] and $[Li(py)SCH_2Ph]_n$.[19] The lowest coordination number observed for lithium in these complexes is 3, and in all cases lithiums are coordinated by donor solvent molecule(s). In the solid state, however, compound **1** was observed to

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Table 2. Atomic Coordinates ($\times 10^4$) for Important Atoms in [{LiSC$_6$H$_3$-2,6-Mes$_2$}$_2$(Et$_2$O)$_2$] (**1**) and Zn(SC$_6$H$_3$-2,6-Mes$_2$)$_2$ (**3**)

	x	*y*	*z*
	Compound **1**		
Li(1)	3175(6)	2880(4)	1615(2)
S(1)	2351(1)	2045(1)	2248(1)
O(1)	4935(3)	2808(2)	1842(1)
O(2)	2832(3)	4026(2)	1498(1)
C(1)	2563(4)	1679(3)	452(1)
C(2)	2737(4)	2025(3)	11(1)
C(3)	3197(5)	1552(4)	−338(2)
C(4)	3436(6)	756(4)	−259(2)
C(5)	3257(5)	410(3)	169(2)
C(6)	2815(4)	861(3)	527(2)
C(7)	2609(5)	471(3)	987(2)
C(8)	1468(5)	124(3)	1042(2)
C(9)	1294(5)	−189(3)	1489(2)
C(10)	2232(5)	−198(3)	1873(2)
C(11)	3355(5)	111(3)	1805(2)
C(12)	3569(4)	452(3)	1370(2)
C(13)	449(5)	105(3)	627(2)
C(14)	2018(6)	−518(4)	2353(2)
C915)	4808(4)	799(3)	1039(2)
Li(2)	1379(7)	1467(5)	1526(3)
S(2)	1988(1)	2265(1)	897(1)
C(25)	1294(3)	2291(2)	2645(1)
C(26)	13(4)	2281(3)	2498(1)
C(27)	−787(4)	2457(4)	2827(2)
C(28)	−367(4)	2625(4)	3299(2)
C(29)	876(4)	2626(3)	3449(2)
C(30)	1716(3)	2464(2)	3132(1)
C(40)	−524(3)	2087(3)	1990(1)
C(41)	−628(3)	2667(3)	1628(1)
C(42)	−1188(4)	2467(3)	1173(2)
C(43)	−1655(4)	1719(3)	1060(2)
C(44)	−1542(4)	1145(3)	1420(2)
C(45)	−980(4)	1316(3)	1884(2)
C(46)	−160(4)	3499(3)	1726(2)
C(47)	−2295(4)	1526(4)	561(2)
C(48)	−878(5)	689(3)	2268(2)
	Compound **3**		
Zn(1)	2795(1)	1376(1)	928(1)
S(1)	2433(1)	26(1)	1269(1)
S(2)	2461(1)	2700(1)	273(1)
C(1)	2476(3)	−795(3)	562(3)
C(2)	2040(3)	−1640(3)	505(3)
C(3)	2077(3)	−2335(3)	−14(3)
C(4)	2537(3)	−2199(3)	−472(3)
C(5)	2958(3)	−1356(3)	−429(3)
C(6)	2935(3)	−656(3)	83(3)
C(7)	3415(3)	233(3)	96(2)
C(8)	3048(3)	876(3)	−532(3)
C(9)	3545(3)	1637(3)	−570(3)
C(10)	4386(3)	1781(3)	0(3)
C(11)	4732(3)	1148(3)	623(3)
C(12)	4263(3)	365(3)	675(3)
C(13)	2132(3)	758(3)	−1142(3)
C(14)	4892(3)	2631(3)	−41(3)
C(15)	4679(3)	−334(3)	1348(3)
C(25)	2520(3)	3545(3)	993(3)
C(26)	2145(3)	4430(3)	693(3)
C(27)	2219(3)	5143(3)	1239(3)
C(28)	2638(3)	5006(3)	2057(3)
C(29)	2995(3)	4137(3)	2341(3)
C(30)	2934(3)	3408(3)	1825(3)
C(31)	3327(3)	2495(3)	2192(2)
C(32)	2878(3)	1911(3)	2518(2)
C(33)	3319(3)	1137(3)	2971(2)
C(34)	4159(3)	924(3)	3092(3)
C(35)	4579(3)	1489(3)	2743(3)
C(36)	4183(3)	2271(3)	2297(3)
C(37)	1951(3)	2102(3)	2379(3)
C(38)	4606(4)	82(4)	3593(3)
C(39)	4671(3)	2906(3)	1973(3)

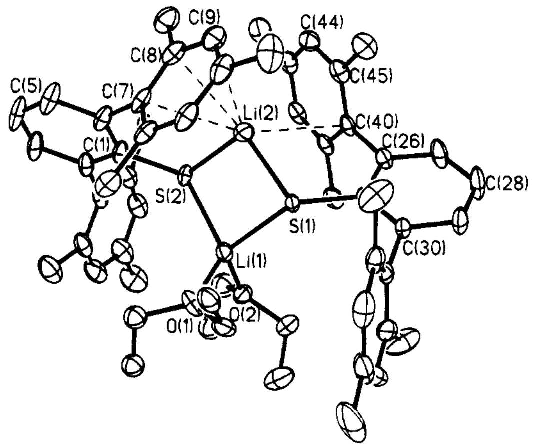

Figure 1. Thermal ellipsoid (30%) drawing of [{LiSC$_6$H$_3$-2,6-Mes$_2$}$_2$-(Et$_2$O)$_2$] (**1**). Hydrogen atoms are omitted for clarity.

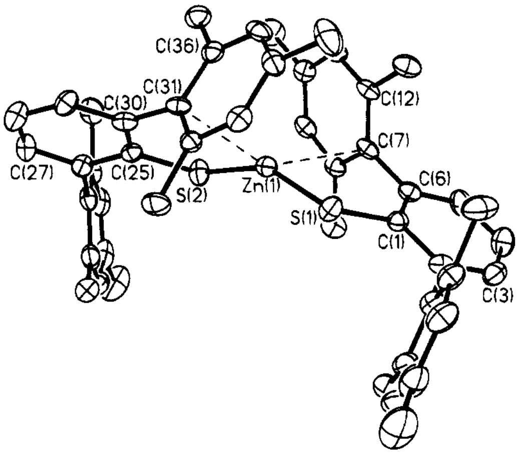

Figure 2. Thermal ellipsoid (50%) drawing of Zn(SC$_6$H$_3$-2,6-Mes$_2$)$_2$ (**2**). Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **1** and **3**

	Compound **1**		
Li(1)—S(1)	2.521(7)	S(1)—Li(1)—S(2)	98.3(2)
Li(1)—S(2)	2.473(7)	S(1)—Li(2)—S(2)	105.2(3)
Li(1)—O(1)	1.951(7)	Li(1)—S(1)—Li(2)	77.7(2)
Li(1)—O(2)	1.977(7)	Li(1)—S(2)—Li(2)	78.4(3)
Li(2)—S(1)	2.366(7)	Li(1)—S(1)—C(25)	130.1(2)
Li(2)—S(2)	2.382(8)	Li(1)—S(2)—C(1)	127.7(2)
Li(2)--C(7)	2.725(7)	Li(2)—S(1)—C(25)	112.3(2)
Li(2)--C(8)	2.637(7)	Si(2)—S(2)—C(1)	111.8(3)
Li(2)--C(9)	2.775(7)	O(1)—Li(1)—O(2)	105.6(4)
Li(2)--C(40)	2.801(7)	O(1)—Li(1)—S(1)	99.6(3)
S(1)—C(25)	1.762(4)	O(1)—Li(1)—S(2)	129.0(4)
S(2)—C(1)	1.769(5)	O(2)—Li(1)—S(1)	125.4(3)
		O(2)—Li(1)—S(2)	101.7(3)
	Compound **3**		
Zn(1)—S(1)	2.199(1)	S(1)—Zn(1)—S(2)	151.7(1)
Zn(1)—S(2)	2.193(1)	Zn(1)—S(1)—C(1)	106.4(2)
S(1)—C(1)	1.772(5)	Zn(1)—S(2)—C(25)	105.6(1)
S(2)—C(25)	1.762(5)	S(1)—C(1)—C(6)	123.9(3)
Zn(1)--C(7)	2.718	S(1)—C(1)—C(2)	117.0(4)
Zn(1)--C(31)	2.651	S(2)—C(25)—C(30)	124.2(3)
		S(2)—C(25)—C(26)	116.6(3)

have two different lithium environments (Figure 1). Thus, Li(2) is solvated by thiolate ligands whereas Li(1) is complexed to two thiolate ligands and two ethers. This results in short Li—S bond lengths and a wide S—Li—S angle at Li(2). Both of these features clearly reflect the less hindered environment and lower coordination at this metal center. The Li—S bond lengths at Li(1) are significantly (*ca.* 0.12 Å) longer than those observed at Li(2). In addition, they are marginally longer than Li—S distances in previously reported lithium thiolate complexes where lithium is four-coordinate, *i.e.* Li(THF)$_3$SMes*[18] and

$Li(py)_3SC_6H_5$-2-Me[19] (2.412(6)−2.508(2) Å). Oddly, the Li(2)—S bond lengths are slightly longer than those found in the complex $[Li_2(THF)_{3.5}\{SC(SiMe_3)_3\}_2]$[17] (2.328(19) and 2.354(19) Å), in which lithium is three-coordinate. The Li(2)--C interactions are considerably longer than the sum of the radii of Li (1.57 Å)[20] and carbon (0.73 Å)[16a] and are also longer than the Li—C distances observed in $[LiC_6H_2$-2,4,6-*i*-$Pr_3]_4$[21] (Li—C = 2.28−2.37 Å), in which lithium interacts with the aromatic rings in an η^6-fashion. The proximity of the mesityl rings to lithium results from weak electrostatic interactions between the electron-rich aryl rings and the positively charged lithium ion. The long Li(2)--C distances and the observation of only one mesityl resonance in the ^1H NMR spectrum (presumably a result of rapid rotation about the S—C bond on the ^1H NMR time scale) suggest that these interactions are weak.

Compound **2** was prepared by the addition of the thiol to dibutylmagnesium and was found to be insoluble in hexane. Crystalline material suitable for X-ray analysis was not obtained from toluene or ether solvents in which the compound is readily soluble. Similarities in the ^1H NMR of **2** and **3** suggest that in solution the magnesium complex is also monomeric.

Compound **3** was synthesized in good yield by treatment of $Zn[N(SiMe_3)_2]_2$ with 2 equiv of HSC_6H_3-2,6-Mes_2. It represents the first structural characterization of a two-coordinate, monomeric zinc thiolate. The monomeric character of **3** is presumably due to the large size of the thiolate ligands. Much of the research involving zinc thiolate complexes has focused on a search for structural models for the metal−sulfur bonding in zinc−cysteine metalloproteins.[22−24] Recent investigations of the structural chararcteristics of low-coordinate zinc thiolates has yielded a variety of structure types, all of which have coordination numbers of 3 or more at zinc.[1,2a,3−8] A number of structures of two-coordinate zinc compounds in the solid state have been reported in the literature;[25−29] however, none has involved main group 6 ligands and only one, $Zn[Si(SiMe_3)_3]_2$,[25] involves direct bonding to heavier main group atoms.

Significant deviation from linear S—Zn—S coordination is observed in the structure of **3**. The S—Zn—S angle of 151.7(1)° implies that the environment at zinc is more open on the side opposite to the sulfurs. Perhaps as a result of this, relatively close Zn--C(ligand) interactions are observed. The Zn—S bond lengths in **3** are similar to the distances found in the T-shaped monomer $Et_2OZn(SMes^*)_2$[6] (*ca.* 2.196 Å) and in dimeric $[Zn(SC_6H_3$-2,6-$(SiMe_3)_2)_2]_2$[30] (2.202(2) Å, terminal Zn—S) and $[Zn(SMes^*)_2]_2$[8] (2.194(5) Å, terminal Zn—S). They are, however, slightly shorter than those observed for the three-coordinate anion $[Zn(SC_6H$-2,3,5-$Me_4)_3]^-$ [2a] (ca. 2.23 Å), and they are *ca.* 0.15 Å shorter than the Zn—S distances observed for $[Zn(SPh)_4]^{2-}$ [2b] (2.362(3) Å). Remarkably, the S—Zn—S angle of 159.6(1)° in three-coordinate $Et_2OZn(SMes^*)_2$[6] is 8° wider than the corresponding angle in **3**. The Zn--C interactions in **3** (≥2.65 Å) are much longer than normal Zn—C bond lengths observed for zinc aryl and alkyl compounds (2.02 Å average).[27,31] As in **1**, the interactions in **3** may result from a weak polar attraction between the electron-poor metal center and electron-rich aryl rings of the ligand. This view is consistent with the structure of the iron compound in which significantly shorter Fe--C contacts (*ca.* 2.5 Å) are observed in spite of the similar radii of iron and zinc (*ca.* 1.25 Å).[32] The aryl ring contacts in the iron species are shorter, perhaps because of the availability of partially occupied low-energy d orbitals at iron (only 10 electrons in the valence shell) in comparison to zinc (14 electrons), where the d orbitals are filled. The influence of the metal−aryl ring interaction upon the geometry at the metal center is consistent with the deviation of the S—M—S angles from 180°. The increased strength of the interaction in the case of iron is reflected in the high degree of distortion from linearity (S—Fe—S is *ca.* 121°) in that compound. It is also notable that in **3** the S—C(ipso)—C(ortho) angles in each ligand differ by about 7°. The wider angle is observed in the case of the ortho mesityl substituent that has the close contacts with zinc. The asymmetry in the angle, which is not observed in the iron or lithium complexes, is probably a consequence of greater steric crowding in **3**. An alternative view of the reasons for the bent geometry at zinc involves the packing of the molecules in the crystal phase and interligand steric interactions, which may determine the amount of bending in the easily distorted S—Zn—S angle, which in turn may determine the strength of the Zn--C interations.

Two-coordinate zinc compounds with relatively large distortions from the expected 180° angles have not been previously described. The structures of $Zn\{N(SiMePh_2)_2\}_2$[26] and $Zn\{C_6H_2$-2,4,6-$(CF_3)_3\}_2$,[27] which have angles at zinc of 177.5(2) and 170.0(1)°, respectively, represent the maximum previously observed deviation from linear geometry in the solid state.

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Supplementary Material Available: Tables giving full details of the crystal data and crystallographic data collections, thermal parameters, bond distances, bond angles, and non-hydrogen atom and hydrogen atom coordinates for **1** and **3** (19 pages). Ordering information is given on any current masthead page. Listings of observed and calculated structure factors for **1** and **3** are available from the authors.

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