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Synthesis and Characterization of the First Three-Coordinate Donor-Free Magnesium Thiolates, $[Mg(STriph)_2]_2$ (Triph = $2,4,6\text{-}Ph_3C_6H_2$) and $[Mg(SMes^*)_2]_2$ (Mes* = $2,4,6\text{-}t\text{-}Bu_3C_6H_2$), and the Four-Coordinate Magnesium Thiolate $Mg(SMes^*)_2(OEt_2)_2$ and Selenolate $Mg(SeMes^*)_2(THF)_2$[1]

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The synthesis and structural characterization of the first three-coordinate dimeric magnesium thiolate $[Mg(STriph)_2]_2$, **1** (Triph = $2,4,6\text{-}Ph_3C_6H_2$), and of the four-coordinate etherates $Mg\{SMes^*\}_2(Et_2O)_2$, **3** (Mes* = $2,4,6\text{-}t\text{-}Bu_3C_6H_2$), and $Mg\{SeMes^*\}_2(THF)_2$, **4**, are described. We also report the synthesis and characterization of the dimeric, presumably three-coordinate Mg thiolate $[Mg(SMes^*)_2]_2$, **2**. Compound **1** is prepared in the reaction of Mg(*n*-Bu/*s*-Bu)$_2$ or $[Mg\{N(SiMe_3)_2\}_2]_2$ with 2 equiv of the bulky thiol HSTriph in toluene. The compound exhibits distorted trigonal-planar geometry at the metal center. Compound **2** is accessible by a reaction analogous to that described for **1**, using HSMes* instead of HSTriph. Although crystallographic data for **2** are not available, the spectroscopic characterization indicates a dimeric species with a distorted trigonal planar environment at Mg. Compound **3** is synthesized by reacting Mg(*n*-Bu/*s*-Bu)$_2$ or alternatively $[Mg\{N(SiMe_3)_2\}_2]_2$ with 2 equiv of the sterically demanding HSMes* in a hexane/diethyl ether mixture. This compound can also be prepared by the reaction of $MgBr_2$ with 2 equiv of the corresponding lithium thiolate in diethyl ether. $Mg\{SeMes^*\}_2(THF)_2$ is prepared by a reaction sequence similar to that described for **3**, by the addition of 2 equiv of freshly prepared HSeMes* in a mixture of hexane and tetrahydrofuran. The reaction of $MgBr_2$ with 2 equiv of lithium selenolate in THF affords **4** in good yield. All compounds were characterized by ^1H NMR and IR spectroscopy, as well as elemental analysis; species **1**, **3**, and **4** were also examined by X-ray crystallography. Crystal data with Mo Kα (λ = 0.710 73 Å) at 213 K (for **1** and **3**) or CuKα (λ = 1.54178 Å) at 130 K for **4** are as follows: **1**, a = 12.055(2) Å, b = 18.341(4) Å, c = 16.635(3) Å, β = 98.75(3)°, V = 3635(2) Å^3, Z = 2, monoclinic, space group $P2_1/n$, 1764 ($I > 2\sigma(I)$) data, R = 0.076; **3**, a = 11.083(2) Å, b = 13.325(3) Å, c = 16.466(3) Å, α = 93.58(3)°, β = 95.00(3)°, γ = 106.41(3)°, V = 2314.1(12) Å^3, Z = 2, triclinic, space group $P\bar{1}$, 6028 ($I > 3\sigma(I)$) data, R = 0.072; **4**, a = 16.956(7) Å, b = 16.425(5) Å, c = 17.915(6) Å, β = 117.30(2)°, V = 4434(2) Å^3, Z = 4, monoclinic, space group $P2_1/n$, 4118 ($I > 2\sigma(I)$) data, R = 0.059.

Introduction

The last decade has witnessed a dramatic increase in the number of structurally characterized alkaline-metal[2] and organomagnesium compounds,[3] many of them exhibiting unique structural features. However, the chemistry of beryllium and the heavier alkaline-earth elements Ca, Sr, and Ba remains an undeveloped area of organometallic research.[4] Work in this field has been limited by the high toxicity of Be and its compounds[5] and the ionic nature of the heavier group 2 elements, which often form insoluble polymers.[4,6,7] Magnesium compounds are the best explored species among the group of alkaline-earth materials. The first synthesis of an organometallic magnesium species was reported as early as 1860.[8] Later these studies were intensified and organomagnesium chemistry was extensively examined by Grignard, who established that organomagnesium reagents play a significant role in synthetic inorganic and organic chemistry.[9] While the chemistry of organomagnesium compounds has been intensely explored over the last century,[3] well-characterized examples of compounds exhibiting other than magnesium−carbon bonds are rare.

More specifically, there are only few structurally characterized compounds in which magnesium is bound to atoms from the second or third row of the periodic table. Furthermore, the majority of structurally characterized Mg species exhibit a coordination number of 4 at Mg; very few species display a coordination number of 3 or lower at the metal center, and these examples are exclusively limited to compounds in which Mg is bound to atoms from the first long row of the periodic table. Such examples of well-characterized magnesium derivatives include the two-coordinate alkyl derivatives $Mg\{CH(SiMe_3)_2\}_2$[10] and $Mg\{C(SiMe_3)_3\}_2$,[11] and the three-coordinate $[Li(THF)_{0.6}$-

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(1) This work is dedicated to Prof. H. Roesky on occasion of his 60th birthday.

(2) See for example: Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353. Gregory, K.; Schleyer, P. v. R. Snaith, R. *Adv. Inorg. Chem.* **1991**, *37*, 47.

(3) See for example: Markies, P. R.; Ackerman, O. S.; Bickelhaupt, F. *Adv. Organomet. Chem.* **1991**, *37*, 47. Coates, G. E.; Green, M. L. H.; Wade, K. *Organometallic Compounds*, 3rd ed.; Methuen: London, 1967.

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$(Et_2O)_{0.4}][Mg(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_3]$.[12] Amido species include the dimeric $[Mg\{N(SiMe_3)_2\}_2]_2$,[13] the etherate $Mg\{N(SiMe_3)_2\}_2(THF)_2$,[14] and the monomeric $Mg\{N(SiPh_2Me)_2\}_2$, which exhibits an unusual N−Mg−N angle of 162.8°.[15] Structurally characterized Mg alkoxides and aryloxides include the dimeric $[Mg\{O(2,6\text{-}t\text{-}Bu_2C_6H_3)\}_2]_2$ and $[Mg\{O(2,6\text{-}t\text{-}Bu_2\text{-}4MeC_6H_2)\}_2]_2$, both exhibiting three-coordinate Mg centers.[16] Other examples include a series of [tris(pyrazolyl)hydroborato]magnesium alkyl derivatives $\{\eta^3\text{-}HB(3\text{-}t\text{-}Bupz)_3\}MgR$ (pz = pyrazolyl) and $\{\eta^3\text{-}HB(3,5\text{-}Me_2pz)_3\}MgR$ (R = CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$, $CH{=}CH_2$, C_6H_5, CH_2SiMe_3)[17] and the peroxo species $\{\eta^3\text{-}HB(3\text{-}t\text{-}Bupz)_3\}MgOOR$ (R = CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$).[18] The structurally uncharacterized but presumably two-coordinate thiolate $Mg\{S(2,6Mes_2C_6H_3)\}_2$,[19] and the four-coordinate tellurolato species $Mg\{TeSi(SiMe_3)_3\}_2(THF)_2$[20] represent examples of species exhibiting Mg bound to heavier organochalcogenides. During the course of preparation of this work for publication, we became also aware of work conducted by Gindelberger and Arnold,[21] who described the synthesis and characterization of alkaline-earth selenolates and tellurolates, including the structural characterization of $Mg\{SeSi(SiMe_3)_3\}_2$-TRMPSI (TRMPSI = (tris(dimethylphosphino)methyl)-*tert*-butylsilane).[21]

Magnesium thiolato, selenolato, and tellurolato species are important starting materials for the preparation of transition metal organochalcogenides, since they are much less reducing than the corresponding alkaline derivatives. Thus, the redox chemistry often observed during the reaction of alkaline thiolates or selenolates with transition metal halides can be avoided.[22] Our goal was to prepare a selection of magnesium thiolato and selenolato derivatives to create a new class of sterically demanding thiolato and selenolato transfer agents for the preparation of transition metal thiolates and selenolates. The chemistry of transition metal thiolates and selenolates exhibiting unusual coordination numbers is an active area of research, reflected in part by the crystal structure analysis of the Fe−Mo cofactor of nitrogenase from *Azotobacter vinelandii* which has revealed six of the seven Fe sites to be three-coordinate.[23] Currently only four iron thiolates displaying three-coordinate metals are known; examples are the dimeric species $[Fe(SR)_2]_2$ (R = Mes*, Triph)[24,25] and the monomeric $PPh_4[Fe(SMes^*)_3]$ and $[Li(THF)_2Fe(SMes^*)_3]$, which are prepared from the dimers by addition of 1 equiv of thiolate.[26] These compounds can not be prepared by common salt elimination reactions between $FeBr_2$ and the corresponding lithium thiolates. With the availability of a variety of sterically demanding magnesium thiolates and selenolates, the synthesis of a wide variety of transition metal−thiolato and −selenolato derivatives may be realized.

We are interested in the coordination geometry of group 2 bis(thiolates) and −(selenolates) and its dependence on the metal and/or ligand size. If small organic groups such as methyl are attached to the chalcogeno atom, polymers which are insoluble in organic solvents are formed. The use of sterically demanding ligands allows the synthesis of monomeric or dimeric species, exhibiting three- or four-coordinate metal centers. Moreover, these compounds are soluble in organic solvents and can be subjected to a variety of analytical methods.

In this paper we describe the synthesis of the first structurally characterized Mg thiolates, including the three-coordinate $[Mg(STriph)_2]_2$, **1**, and the four-coordinate etherate $Mg(SMes^*)_2(Et_2O)_2$, **3**. We also report the synthesis, characterization, and structural analysis of $Mg(SeMes^*)_2(THF)_2$, **4**, one of two Mg selenolates reported to date. Additionally, we describe the synthesis and characterization of $[Mg(SMes^*)_2]_2$, **2**, prepared in nondonating solvents or by keeping **3** under vacuum for several hours. The compound presumably exhibits a dimeric structure with distorted trigonal-planar metal centers.

Experimental Section

General Procedures. All reactions were performed under purified nitrogen atmosphere by using either modified Schlenk techniques or a Braun Labmaster 100 dry box. *n*-Hexane, diethyl ether, and THF were freshly distilled from Na/K alloy and degassed two times before use. Commercially available $Mg(n\text{-}Bu/s\text{-}Bu)_2$ (a 1 M solution in heptane of a 1:1 mixture of the Mg−*n*-butyl and −*s*-butyl derivative), *n*-BuLi (1.6 *m* solution in hexanes), and $MgBr_2$ were used as received. HSTriph,[25] HSMes*,[27] HSeMes*,[28] and $[Mg\{N(SiMe_3)_2\}_2]_2$[14] were synthesized by following literature procedures. ^1H NMR spectra were obtained at 300 MHz in C_6D_6 on a GE QE-300 spectrometer. Infrared spectra were recorded as Nujol mulls between KBr plates, using a Perkin-Elmer PE 1600 FT-IR spectrometer.

Synthesis of $[Mg(STriph)_2]_2$, 1. A quantity of $Mg(n\text{-}Bu/s\text{-}Bu)_2$ (1 mL of a 1 *m* solution) was dissolved in 5 mL of toluene, and 2 mmol of the thiol HSTriph (0.68g), dissolved in 20 mL of toluene, was added slowly via cannula. The pale yellow solution was stirred at room temperature for 18 h and filtered over a Celite padded filter frit. The volume of the solution was reduced to 15 mL to initiate crystallization. After storage at −20 °C, pale yellow crystals of **1** were obtained in 79% yield (0.55g). Mp: dec > 300 °C. The compound can also be obtained by the reaction of $[Mg\{N(SiMe_3)_2\}_2]_2$ with 2 equiv of HSTriph in toluene. Analytical results are identical. δ, ^1H NMR (C_6D_6): 7.10−7.26 (br m, *o*-H), 7.34−7.53 (br m, *p*-H), 7.77 (s, *m*-H). IR (cm^{-1}): 1598 w, 1463 s, 1378 s, 1308 w, 1157 w, 1109 m, 1109 m, 1072 m, 1027 m, 888 m, 837 m, 758 s, 741 s, 651 m, 627 m, 612 s, 602 sh, 522 sh, 498 s, 479 sh. Anal. Calcd (found): C, 82.5 (82.1), H, 4.9 (4.8).

Synthesis of $[Mg(SMes^*)_2]_2$, 2. The compound is available by the reaction of $Mg(n\text{-}Bu/s\text{-}Bu)_2$ or alternatively $[Mg\{N(SiMe_3)_2\}_2]_2$ with 2 equiv of the sterically demanding thiol HSMes* in toluene. Complex **2** can also be obtained by subjecting **3** to an oil pump vacuum for several hours or heating **3** to 100 °C for 1 h; the subsequent loss of diethyl ether can be monitored by ^1H NMR spectroscopy. The analytical data for the product prepared by either route are identical. The yields are typically around 80−90%. Mp: 195 °C. δ, ^1H NMR (C_6D_6): 7.55 (s, 2H, *m*-H), 1.60 (s, 18H, *o*-*t*-Bu), 1.29 (s, 9H, *p*-*t*-Bu). IR (cm^{-1}): 1593 m, 1549 w, 1460 s, 1378 s, 1361 s, 1284 w, 1260 m, 1240 s, 1214 s, 1184 m, 1157 m, 1096 w, 1038 s, 923 w, 877 s, 804

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m, 173 m, 729 s, 695 w, 646 w, 608 s, 544 w, 495 m, 463 s. Anal. Calcd (found): C, 75.4 (74.9); H, 10.2 (10.0).

Synthesis of $Mg(SMes^*)_2(OEt_2)_2$, 3. HSMes* (2 mmol, 0.557g) was dissolved in 20 mL of *n*-hexane and 10 mL of diethyl ether. A 1 mL portion of $Mg(s\text{-}Bu/n\text{-}Bu)_2$ (1 mmol) or, as an alternate reaction route, 1 mmol of $[Mg\{N(SiMe_3)_2\}_2]_2$ in 15 mL of *n*-hexane was added slowly via syringe or cannula at room temperature. The resulting pale yellow solution was stirred for 18 h at room temperature, during which it became cloudy. All volatiles were removed in vacuum. The resulting white solid was recrystallized from a mixture of 30 mL of hexane and 5 mL of diethyl ether. Upon reduction of the volume to 15 mL and storage at room temperature, 0.5 g of colorless crystals was isolated (69% yield). Mp: colorless crystals turn white at >100 °C (loss of diethyl ether); the resulting white material decompose at >180 °C. δ, ^1H NMR (C_6D_6): 7.49 (s, 2H, *m*-H), 3.45 (q, 4H, Et_2O), 1.86 (s, 18H, *o-t*-Bu), 1.41 (s, 9H, *p-t*-Bu), 0.78 (t, 6H, Et_2O). IR (cm^{-1}): 1595 m, 1460 s, 1411 m, 1378 s, 1261 m, 1215 w, 1021 m, 878 m, 802 m, 722 m. Anal. Calcd (found) C, 72.6 (72.2); H, 10.9 (10.7).

Synthesis of $Mg(SeMes^*)_2(THF)_2$, 4. Freshly reduced HSeMes* (0.8 g, 2.45 mmol) was dissolved in a solvent mixture of 20 mL of *n*-hexane and 10 mL of tetrahydrofuran. A 1.22 mL portion of $Mg(s\text{-}Bu/n\text{-}Bu)_2$ (1.22 mmol) was slowly added using a syringe. The pale yellow solution was stirred for 18 h at room temperature and then filtered. Reducing the volume of the solution to 10 mL and storage at −20 °C afforded large colorless crystals suitable for single-crystal X-ray analysis. An analogous reaction using $[Mg\{N(SiMe_3)_2\}_2]_2$ with 2 equiv of HSeMes* or the reaction of $MgBr_2$ with 2 equiv of the corresponding lithium selenolate in a hexane/tetrahydrofuran mixture resulted in analytically pure **4**. Mp: dec >200 °C (pale yellow crystals turn dark yellow). δ, ^1H NMR (C_6D_6): 7.43 (s, 2H, *m*-H), 3.28 (q, 4H, THF), 1.97 (s, 18H, *o-t*-Bu), 1.33 (s, 9H, *p-t*-Bu), 1.28 (t, 4H, THF). IR (cm^{-1}): 1583 w, 1460 s, 1374 s, 1261 m, 1211 w, 1098 m, 1017 s, 917 w, 872 m, 804 m, 740 w, 722 m, 645 w. Anal. Calcd (found): C, 64.7 (64.9); H, 9.2 (9.3).

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 highly viscous hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and quickly placed in the low-temperature nitrogen stream of the diffractometer.[29] Intensity data sets for **1** and **3** were collected at 213 K with the use of a Rigaku AFC5S diffractometer (Mo Kα radiation, $\lambda = 0.710\,73$ Å) equipped with a graphite monochromator and a Molecular Structure Corp. LT device for low-temperature work. Three standard reflections were measured every 150 reflections and showed in all cases only statistical variation of the intensity (<1.5%). Compound **4** was collected at 130 K using a Siemens P4RA diffractometer (Cu Kα radiation, $\lambda = 1.541\,78$ Å), equipped with a Ni filter and locally modified LT-2 low-temperature device. Two standard reflections showed only statistical variation. The intensities of all data sets were corrected for Lorentz and polarization effects; extinction was disregarded. Absorption effects in **3** were corrected using semiempirical ψ scans; absorption in **4** was corrected using the program XABS.[30] Absorption effects in **1** were disregarded, due to a weak data set. Crystallographic programs used for structure solution and refinement were those of the SHELXTL-Plus package installed on a PC clone.[31] Scattering factors were those provided with the SHELX program system. Some details of the data collections and refinements are given in Table 1; coordinates of selected atoms are provided in Table 2. Important bond lengths and angles are given in Tables 3 and 4. Further details are provided in the supplementary material.

Table 1. Summary of Data Collection, Structure Solution, and Refinement of $[Mg\{S(2,4,6\text{-}Ph_3C_6H_2)\}_2]_2$, **1**, $Mg\{S(2,4,6\text{-}t\text{-}Bu_3C_6H_2)\}_2(Et_2O)_2$, **3**, and $Mg\{Se(2,4,6\text{-}t\text{-}Bu_3C_6H_2)\}_2(THF)_2$, **4**

	1	**3**	**4**
formula	$C_{96}H_{68}Mg_2S_4$	$C_{44}H_{78}MgO_2S_2$	$C_{44}H_{74}MgO_2Se_2$
fw	1398.4	727.5	817.3
crystal descripn	colorl plate	colorl block	colorl paralellepiped
a, Å	12.055(2)	11.083(2)	16.956(7)
b, Å	18.341(4)	13.325(3)	16.425(5)
c, Å	16.635(3)	16.466(3)	17.915(6)
α, deg	90	93.58(3)	90
β, deg	98.75(3)	95.00(3)	117.3(2)
γ, deg	90	106.41(3)	90
V, $Å^3$	3635(2)	2314(12)	4434(2)
Z	2	2	4
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
d_{calc} g/cm^3	1.279	1.044	1.224
lin abs coeff, cm^{-1}	1.98	1.59	2.456
radiation	Mo Kα	Mo Kα	Cu Kα
T, K	213	213	130
2θ range, deg	0−45	0−50	0−115
no. of obsd reflns	1764	6028	4118
no. of variables	220	436	442
R,[a] R_w[b]	0.076, 0.072	0.072, 0.079	0.059, 0.064

[a] $R = \sum||F_o| - |F_c||/|F_o|$. [b] $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$.

Table 2. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for Significant Atoms in $[Mg\{S(2,4,6\text{-}Ph_3C_6H_2)\}_2]_2$, **1**, $Mg\{S(2,4,6\text{-}t\text{-}Bu_3C_6H_2)\}_2(Et_2O)_2$, **3**, and $Mg\{Se(2,4,6\text{-}t\text{-}Bu_3C_6H_2)\}_2(THF)_2$, **3**

atom	*x*	*y*	*z*	*U*
		Compound 1		
Mg(1)	1432(3)	9872(2)	4848(2)	45(2)
S(1)	406(3)	10657(2)	5688(2)	45(1)
S(2)	3056(3)	9157(2)	5163(2)	51(1)
C(1)	640(9)	10617(6)	6767(6)	39(3)
C(8)	−997(10)	9263(6)	6363(6)	49(3)
C(25)	2237(9)	8381(6)	5380(7)	45(3)
		Compound **3**		
Mg(1)	1687(1)	636(1)	7993(1)	34(1)
S(1)	3622(1)	1463(1)	7467(1)	34(1)
S(2)	−209(1)	998(1)	8340(1)	34(1)
O(1)	1202(3)	−838(2)	7354(2)	55(1)
O(2)	2290(3)	113(2)	9065(2)	48(1)
C(1)	3997(3)	2859(3)	7412(2)	27(1)
C(19)	−758(3)	1917(3)	7756(2)	27(1)
		Compound **4**		
Mg(1)	9378(2)	3154(2)	1831(2)	25(1)
Se(1)	9332(1)	2131(1)	759(1)	23(1)
Se(2)	8566(1)	4507(1)	1409(1)	24(1)
O(1)	9033(4)	2475(3)	2577(3)	38(3)
O(2)	10644(3)	3369(3)	2680(3)	30(2)
C(1)	10426(5)	2407(4)	702(5)	22(3)
C(7)	7967(5)	4544(4)	2118(4)	22(3)

X-ray-quality crystals for **1** were grown from a concentrated toluene solution by placing the reaction vessel in an acetone-filled Dewar flask which was slowly cooled to −20 °C. X-ray-suitable crystals of **3** and **4** were grown from diethyl ether or a tetrahydrofuran/hexane mixture stored at −20 °C. The crystal structures of **1, 3,** and **4** were solved by direct methods; missing atoms were located in several difference Fourier cycles and included in subsequent refinement cycles. The structures were refined using methods based on full-matrix least-squares refinement on $|F_o|$. The function minimized was $[\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. In all cases, hydrogen atoms were included by the use of a riding model with C−H distances of 0.96 Å and fixed isotropic thermal parameters of 0.06 Å for **1**, 0.05 Å for **3**, and 0.08 Å for **4**. In **1**, only the Mg and the two sulfur atoms were refined using anisotropic thermal parameters; in **3** and **4**, all non-hydrogen atoms, except those in disordered positions, were refined this way. In **3**, both *p-t*-Bu groups at the ligand were found to be disordered and were included in the refinement using 50% split positions.

Results and Discussion

Structural Descriptions. $[Mg(STriph)_2]_2$, 1. Selected bond angles and distances are provided in Table 3. As shown in

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(29) Hope, H. In *ACS Symposium Series 357*; Wayda, A. L., Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, Chapter 10, p 257.

(30) Absorption correction program XABS: Moezzi, B. Ph.D. Dissertation, University of California, Davis, 1987. The program obtains an absorption tensor from $F_o - F_c$ differences.

(31) Sheldrick, G. M. SHELXTL-Plus. A program package for crystal structure solution and refinement. University of Göttingen, 1992.

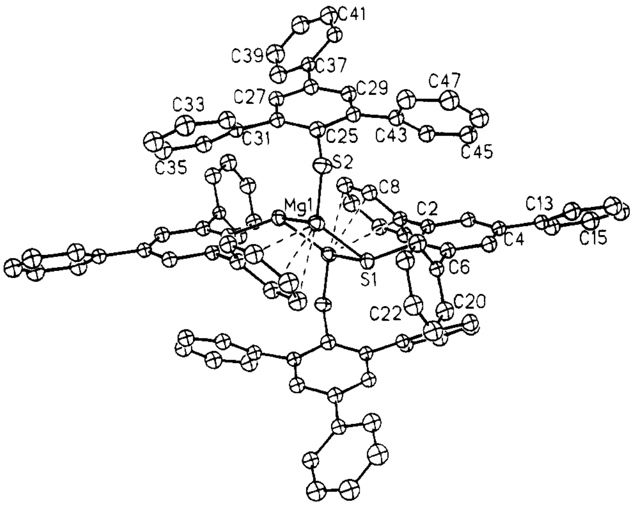

Figure 1. Computer-generated plot of **1** (35% ellipsoids). Hydrogen atoms have been omitted for clarity. Dashed lines indicate Mg−C contacts within the range of van der Waals contacts; see text.

Table 3. Comparison of Important Bond Lengths (Å) and Angles (deg) in $[Mg\{S(2,4,6\text{-}Ph_3C_6H_2)\}_2]_2$, **1**, and the Isomorphous Species $[Fe\{S(2,4,6\text{-}Ph_3C_6H_2)\}_2]_2$[25]

	$[Mg\{STriph\}_2]_2$	$[Fe\{STriph\}_2]_2$
$M-S_{br}$	2.466(5)	2.378(3)
$M-S_{br}$	2.458(5)	2.337(3)
$M-S_t$	2.349(5)	2.262(3)
$S_{br}-M-S_{br}$	86.2(2)	97.1(1)
S_t-M-S_{br}	132.3(2)	129.5(1)
	122.3(2)	120.7(1)
$M-S_{br}-C$	122.1(4)	118.5(3)
$M-S_{br}-M$	93.8(2)	82.9(1)
$M-S-C$	91.3(4)	92.5(3)
$\Sigma°M$	340.8	347.3
$\Sigma°S$	326.2	310.6
$M-C$	2.555	2.529
	2.797	2.717
$M-M$	3.595	3.121

Table 4. Comparison of Important Bond Lengths (Å) and Angles (deg) in $Mg\{S(2,4,6\text{-}t\text{-}Bu_3C_6H_2)\}_2(OEt_2)_2$, **3**, and $Mg\{Se(2,4,6\text{-}t\text{-}Bu_3C_6H_2)\}_2(THF)_2$, **4**

	$Mg(SMes^*)_2(OEt_2)_2$	$Mg(SeMes^*)_2(THF)_2$
$Mg-E$	2.382(2)	2.536(3)
	2.392(2)	2.539(3)
$Mg-H$	2.074(3)	2.021(5)
	2.065(3)	2.013(5)
$E-C$	1.798(4)	1.958(9)
	1.807(4)	1.957(10)
$E-Mg-E$	140.4(1)	122.1(1)
$O-Mg-O$	93.5(1)	97.4(2)
$Mg-E-C$	116.6(1)	100.7(2)
	117.1(1)	101.8(2)

Figure 1, **1** is dimeric with thiolato bridges and terminal thiolato groups. The halves of the dimer are related by a center of symmetry, such that the core Mg_2S_2 array is required to be planar. However, the $\{MgS_3\}$ coordination at the metal deviates from planarity with the sum of the S−Mg−S angles of 340.8°. In addition, the S−Mg−S angles are very irregular with values ranging from 86.2(2)° for $S_{br}-Mg-S_{br}$ to 122.3(2) and 132.3(2)° for the angles between the terminal (t) and the bridging (br) thiolato functions. The Mg−S bridging distances are, as expected, longer than the $Mg-S_t$ bond length with values differing by 0.12 Å (2.349(5) *vs* 2.466(5) Å). The sulfur atoms at the thiolato bridges are pyramidally coordinated, the sum of angles being 326.2°. The Mg−S−C angle at the terminal bonded sulfur atom is 91.3°. There are some short interactions

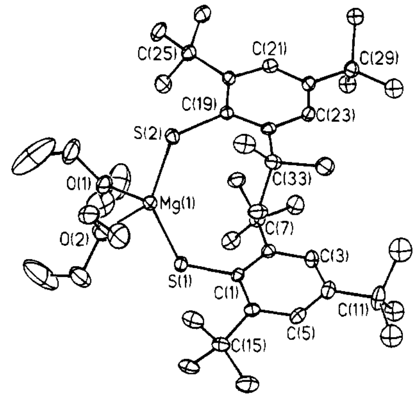

Figure 2. Computer-generated plot of **3** (35% ellipsoids). Hydrogen atoms have been omitted for clarity.

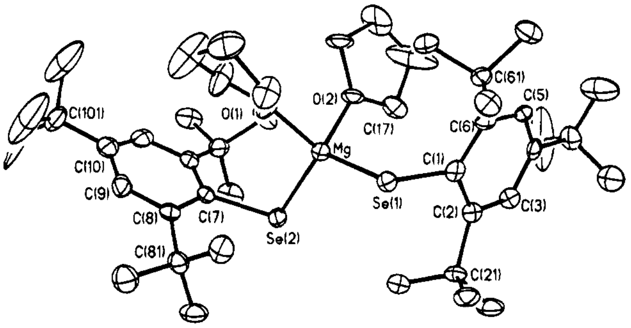

Figure 3. Computer-generated plot of **4** (35% ellipsoids). Hydrogen atoms have been omitted for clarity.

between the magnesium and the carbon atoms of the phenyl ortho ligands, the shortest being 2.555 and 2.797 Å.

$Mg(SMes^*)_2(OEt_2)_2$, 3. The structure of **3** is presented in Figure 2, while important geometrical features of the molecule are listed in Table 4. Compound **3** consists of neutral, discrete monomeric molecules with no crystallographically imposed symmetry. The Mg atom shows a severely distorted tetrahedral geometry, with angles ranging from 93.5(1) to 140.4(1)°. The largest angles are found between the two sterically demanding thiolato groups; the smallest, between the two O atoms of the ether molecules. The two Mg−S distances are very similar at 2.382(2) and 2.392(2) Å; the Mg−O distances are 2.065(3) and 2.074(3) Å, respectively. The shortest Mg−H distances are 2.685 (H8C) and 2.881 Å (H34B), with both H atoms located at *o*-*t*-Bu positions of the thiolato ligand. The S−C distances are 1.798(4) and 1.807(4) Å, with angles at S of 116.6(1) and 117.1(1)°.

$Mg(SeMes^*)_2(THF)_2$, 4. The structure of **4** is shown in Figure 3; important bond lengths and angles are presented in Table 4, together with those of **3** to allow a direct comparison of the two structurally similar molecules. The magnesium atom exhibits a distorted tetrahedral environment with angles ranging from 97.4(2) to 122.1(1) Å. The Mg−Se distances are almost identical with values of 2.526(3) and 2.539(3) Å. The average Se−C distance is 1.96(1) Å; the angles at Se are 100.7(2) and 101.8(2)°.

Discussion

Compounds **1**−**4** were synthesized in good yields in a straightforward manner. $[Mg(STriph)_2]_2$ was obtained by the treatment of Mg(*n*-Bu/*s*-Bu)$_2$ with 2 equiv of the sterically demanding thiol HSTriph in toluene with the concomitant elimination of *n*-Bu/*s*-BuH. Compound **2** is prepared with the bulky thiol HSMes* in an analogous reaction sequence. The compounds may also be prepared from the reaction of the magnesium amide $[Mg\{N(SiMe_3)_2\}_2]_2$ and HSR (R = Mes* and Triph) in non-coordinating solvents:

$$2Mg(n\text{-}Bu/s\text{-}Bu)_2 + 4HSR \rightarrow [Mg(SR)_2]_2 + 4n\text{-}Bu/s\text{-}BuH$$

$$2[Mg\{N(SiMe_3)_2\}_2]_2 + 4HSR \rightarrow [Mg(SR)_2]_2 + 4HN(SiMe_3)_2$$

$$R = 2,4,6\text{-}Ph_3C_6H_2,\ 2,4,6\text{-}t\text{-}Bu_3C_6H_2$$

If the reaction is carried out in the presence of ethers, the monomeric four-coordinate magnesium bis(thiolate etherate) $Mg(SMes^*)_2(Et_2O)_2$, **3**, is obtained. A similar reaction route utilizing 2 equiv of freshly prepared HSeMes* and 1 equiv of $Mg(n\text{-}Bu/s\text{-}Bu)_2$ or $[Mg\{N(SiMe_3)_2\}_2]_2$ in a tetrahydrofuran/hexane mixture yields the monomeric four-coordinate magnesium bis(selenolate etherate) **4**.

$$Mg(n\text{-}Bu/s\text{-}Bu)_2 + 2HER \xrightarrow{\text{ether}} Mg(ER)_2(\text{ether})_2 + 2n\text{-}Bu/s\text{-}BuH$$

$$[Mg\{N(SiMe_3)_2\}_2]_2 + 4HER \xrightarrow{\text{ether}} 2Mg(ER)_2(\text{ether})_2 + 4HN(SiMe_3)_2$$

$$R = 2,4,6\text{-}t\text{-}Bu_3C_6H_2;\ E = S, Se;$$
$$\text{ether} = \text{THF, diethyl ether}$$

The protonolysis reaction between HER (E = S, Se, Te; R = $2,4,6\text{-}t\text{-}Bu_3C_6H_2$, $2,4,6\text{-}Ph_3C_6H_2$, $Si(SiMe_3)_3$)) and main-group or transition-metal amides provides an easy and well-documented access route to the corresponding main-group and transition-metal organochalcogenides.[20–22,24,25,32]

The overall structure of **1** is quite similar to that of its isomorphous iron analog $[Fe\{STriph\}_2]_2$,[25] as shown by the comparison of structural features in Table 3. Both molecules are dimers with two $M\{SR\}_2$ units associated through thiolato bridges. A remarkable feature of both the iron and the magnesium compounds is the short M–C interactions between the metal center and the carbon atoms at the phenyl ortho groups of the Triph ligand. The $Mg-C_{phenyl}$ and $Fe-C_{phenyl}$ distances are quite similar, with the shortest M⋯C contacts at 2.550 and 2.797 Å in **1** and at 2.529 and 2.717 Å in $[Fe(STriph)_2]_2$. These values are well in the range of van der Waals interactions, and apparently the π-type interaction stabilizes the low-coordinate metal centers. A similar contact was observed in the quasi-two-coordinate manganese bis(selenolate) $Mn\{Se(2,6Mes_2C_6H_3)\}_2$ (Mes = $2,4,6\text{-}Me_3C_6H_2$) (Mn–C 2.696, 2.716 Å)[33] and the quasi-two-coordinate iron bis(thiolate) $Fe\{S(2,6\text{-}Mes_2C_6H_3)\}_2$ (Fe–C 2.470, 2.535 Å).[34] Although the crystal structure of $[Mg(SMes^*)_2]_2$, **2**, has not been determined, preliminary data indicate close structural similarities between **2** and its iron and manganese analogues.[24] The iron species $[Fe(SMes^*)_2]_2$ consists of dimeric units with a distorted trigonal-planar geometry at the Fe center. Due to the absence of phenyl groups at the ortho position of the ligand, the π-type interaction observed in **1** is not possible. However, we have not been able to grow X-ray-quality crystals to confirm this assignment.

The solid state structures of $Mg(SMes^*)_2(Et_2O)_2$, **3**, and $Mg(SeMes^*)_2(THF)_2$, **4**, display very similar structural features and exhibit distorted tetrahedral environments at the Mg centers. However, quite different degrees of distortion are observed, indicating the larger effective bulk of the thiolato *versus* the selenolato ligand. The Mg–S and Mg–Se bond lengths are shorter than the values derived from the sum of atomic radii (Mg = 1.60 Å, S = 1.02 Å, Se = 1.117 Å),[35] suggesting that these bonds are of a σ-type with a strong ionic component. This view is consistent with the bond length estimates generated from the sum of atomic radii, corrected for ionic contribution. The sums of atomic radii are 2.602 (Mg–S) and 2.77 Å (Mg–Se); after ionic correction using the Shoemaker–Stevenson formula,[36] theoretical bond distances of 2.511 and 2.657 Å are obtained. These values are significantly longer than those observed in **1**, **3**, or **4**. It is very probable that, since the atomic radius of Mg has been derived from the solid state structure, in which Mg is 12-coordinate, a lower value than 1.60 Å for the Mg radius is more appropriate for the more common coordination number (i.e. 4) observed for molecular Mg compounds. This view is in agreement with experimental data: the Mg–S bond length of the only other structurally characterized compound exhibiting a Mg–S moiety, $[(CuMes)_4(\mu\text{-}SAr)_2(MgSAr)_2]$ (Ar = $2\text{-}((CHMe)NMe_2)C_6H_4$), is 2.389 Å for the four-coordinate Mg center,[37] a value within experimental error of the Mg–S bond length found in **3** (2.387(2) Å). The Mg–Se distances observed in **4** ($2.537(6)_{av}$ Å) are slightly longer than those observed in $Mg\{SeSi(SiMe_3)_3\}_2TRMPSI$ ($2.49(2)_{av}$ Å),[21] which displays a geometry similar to that of **4**. The slightly shorter bond length observed in $Mg\{SeSi(SiMe_3)_3\}_2TRMPSI$ can be rationalized by reduced steric requirements of the $Si(SiMe)_3$ *versus* the Mes* ligand. A comparison of Mg–S bond lengths in the three-coordinate **1** and the etherate **3** shows that the value of (2.387(2) Å) in **3** is intermediate between the terminal (2.349(5) Å) and bridging (2.462(5) Å) Mg–S distances observed in the dimeric **1**. The large Mg–S–C angles in **3** ((116.6(1) and 117.1(1)°) reflect the wide array of possible M–S–C angles reported to date. There is no apparent direct correlation between bond characteristics or degree of ligand bulk and metal–S–C angle, an observation consistent with the variety of M–S–C angles reported: 106.2(2) and 108.7(3)° for the monomeric Fe thiolate $Fe\{S(Mes_2C_6H_3)\}_2$,[24] 115.5(9)° for the cadmium thiolate $(NEt_4)_2\ [Cd(o\text{-}S(SiMe_3)C_6H_4)_4]$,[38] 106.2(6)° for the beryllium thiolate $Be\{SMes^*\}_2OEt_2$,[39] and 98.7(1) up to 103.9(1)° for the aluminum and gallium tris(thiolates) $M(SMes^*)_3$ (M = Al, Ga).[40] The closest Mg–H interactions in **3** are 2.685 (H8C) and 2.881 Å (H34B), involving the hydrogen atoms located on the *tert*-butyl groups of the thiolato ligands. No significant Mg–H contacts are observed in **4**.

If **3** and **4** are left in vacuum at room temperature for several hours or if the compounds are heated above 100 °C (**3**) or 200 °C (**4**), loss of coordinated ether is observed. This process can be monitored by ^1H NMR spectroscopy. After 18 h in vacuum, no ether can be detected in the ^1H NMR spectrum. The

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(32) See for example: Seligson, A. L.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 8214. Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 3478.

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(34) Ellison, J. J.; Ruhlandt-Senge, K.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1178.

(35) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford Science Publications: Oxford, U.K., 1984; p 1288.

(36) Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* **1941**, *63*, 37.

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(39) Ruhlandt-Senge, K.; Bartlett, R. A.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 1724.

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difference in temperature required to induce the removal of ether molecules in **3** and **4** might be related to the strength of the metal−oxygen interaction, as suggested by the significantly shorter Mg−O bonds ($\Delta = 0.053$ Å) observed in the selenolate compound **4** (2.074(3), 2.065(3) Å (**3**) *vs* 2.021(5), 2.013(5) Å (**4**)). This observation is consistent with more effective shielding of the metal center by the thiolato ligand than by the selenolato ligand.

Conclusion

A series of new magnesium compounds containing bonds to heavier group 16 elements has been prepared and characterized. Compounds **1** and **3** are the first Mg thiolates to be structurally characterized to date. $[Mg(STriph)_2]_2$ displays a rare, dimeric structure with three-coordinate metal centers. Analytical and spectroscopic data indicate a dimeric structure for **2**, similar to that observed in $[M\{SMes^*\}_2]_2$ (M = Fe, Mn).[24] However, a definite structural characterization has not been possible to date. $Mg\{SeMes^*\}_2(THF)_2$ and $Mg\{SeSi(SiMe_3)_3\}_2TRMPSI$,[21] provide unique examples of structurally characterized Mg selenolates.

Alkaline-earth bis(organochalcogenides) display σ-type bonds with a high degree of ionic character. If coordinating solvents or bases are used, alkaline-earth bis(organochalcogenides) display coordination numbers of 4−7 at the metal center, depending on the alkaline-earth element, the chalcogen atom, and the size of the R group attached to the chalcogeno atom. A comparison of metal−S or metal−Se bond distances of species with different R groups attached to S or Se clearly shows that the Mes* group exerts a larger steric influence with respect to M−X bond lengthening than the $Si(SiMe_3)_3$ substituent. Work is in progress on the preparation of "donor-deficient" group 2 organochalcogenides and the synthesis of transition metal thiolates and selenolates utilizing the novel magnesium organochalcogenide transfer agents.

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Supplementary Material Available: Full tables of data collection parameters, atom coordinates, bond distances, bond angles, and hydrogen coordinates (27 pages). Ordering information is given on any current masthead page.

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