Novel Structural Principles in Magnesium Thiolate Chemistry: Monomers, Trimers, and the First Magnesiate Thiolate

Scott Chadwick,[†] Ulrich Englich,[†] Mathias O. Senge,[‡] Bruce C. Noll,[§] and Karin Ruhlandt-Senge*,[†]

Department of Chemistry 1-014 Center for Science and Technology, Syracuse University, Syracuse, New York 13244-4100, Institut für Organische Chemie, WE02, Freie Universität Berlin, Takustrasse 3, D-14195 Berlin, Germany, and Department of Chemistry and Biochemistry, University of Colorado at Boulder, Boulder, Colorado 80309-0215

The synthesis and characterization of a family of magnesium thiolates $[Mg(SR)_2(donor)_n]_m$ (R = C_6H_5, C_6F_5, -2-NC_5H_4; $n = 1-4$; $m = 1$, 3) and the first magnesiate thiolate $[cat]_2[Mg(SC_6F_5)_4]$ are described. $Mg(SC_6F_5)_2(py)_3$, **1** (py = pyridine), $Mg(SPh)_2(py)_4$, **2**, the trimer $Mg_3(\mu_2$-$SPh)_6(py)_6$, **3**, the intramolecularly stabilized monomer $Mg(S$-2-$NC_5H_4)_2(py)_2$, **4**, and the "ate" complex [2,6-lutidineH]$_2$[Mg(SC$_6$F$_5$)$_4$], **5**, were synthesized by treating $(C_4H_9)_2Mg$ with HSC$_6$F$_5$, HSC$_6$H$_5$, or HS-2-NC$_5$H$_4$ under addition of pyridine or 2,6-dimethylpyridine. The target molecules were characterized by IR and, depending on solubility, ^{1}H NMR and ^{13}C NMR spectroscopy, melting point, and single-crystal X-ray crystallography. It is clearly shown that the structural chemistry, and therefore the physical properties of the magnesium thiolates, can be influenced by ligand and donor choice, as exemplified by the significant structural variations observed. Use of HSC$_6$F$_5$ and pyridine resulted in the formation of five-coordinate $Mg(SC_6F_5)_2(py)_3 \cdot C_6H_5CH_3$, **1a**, and the solvent-free $Mg(SC_6F_5)_2(py)_3$, **1b**; while utilization of HSC$_6$H$_5$ and pyridine resulted in the formation of the six-coordinate species $Mg(SPh)_2(py)_4$, **2**, and $Mg_3(\mu_2$-$SPh)_6(py)_6$, **3**. Interestingly, compounds **2** and **3** are isolated from almost identical reaction mixtures and are related by an equilibrium: addition of large amounts of pyridine results in the formation of **2** while reduced amounts of donor allow the isolation of the novel trimer **3**. The intramolecularly stabilized, distorted-octahedral complex $Mg(S$-2-$NC_5H_4)_2(py)_2$, **4**, becomes available if 2-mercaptopyridine is used in conjunction with pyridine. A rare example of an anionic alkaline-earth derivative, the tetrahedrally coordinate [2,6-lutidineH]$_2$[Mg(SC$_6$F$_5$)$_4$], **5**, is accessible by treating $(C_4H_9)_2Mg$ with 4 equiv of HSC$_6$F$_5$ and adding 2,6-lutidine.

Introduction

Alkaline-earth chemistry has been revived over the past decade by the discovery of alkaline-earth-containing high-temperature superconductors and ferroelectric materials.[1−3] Since then, a large amount of work has been devoted toward the development of oxygen containing strontium and barium precursors.[4−7] In contrast, the lighter alkaline-earth and the heavier chalcogen congeners have not received much attention, which is surprising considering their importance in wide band gap semiconductors,[8−11] two-color IR optical windows,[12] and phosphor materials.[13] Their use in synthetic chemistry has also been documented.[14−16]

[†] Syracuse University.
[‡] Freie Universität Berlin.
[§] University of Colorado at Boulder.
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To date, materials for wide band gap semiconductors have been based mainly on combinations of group IIB (Zn, Cd) and group VIA (S, Se, Te) elements and their mixed compounds.[17-20] As shown recently, the band gap of the conventional IIB−VIA materials can be widened significantly by alkaline-earth-metal inclusion, as demonstrated with the incorporation of magnesium into ZnS/ZnSe phases. The novel, quaternary ZnMgSSe materials made possible the first continuous-wave operation of blue-green laser diodes at room temperature.[8-11] Functional II−VI magnesium-doped quaternary phases depend critically on precise control of material composition and purity. Much work has been devoted toward the development of suitable routes and precursors, but the high-purity II−VI materials needed for the production of blue green lasers is still difficult to obtain and further work is needed to develop alternative precursors and deposition techniques.

Potential precursor molecules for the quaternary ZnMgSSe materials include magnesium thiolates and selenolates. Their thermal decomposition would result in metal sulfides or selenides and the corresponding thio- or seleno ethers, as shown previously with zinc, cadmium, and lanthanide analogues.[21]

$$Mg(ER)_2 \xrightarrow{\Delta} MgE + RER \qquad (1)$$
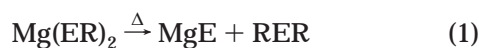
$$E = S, Se; R = aryl, alkyl$$

The importance of alkaline-earth chalcogenolates also extends toward applications in synthetic chemistry. Specifically, magnesium thiolates, selenolates, and tellurolates are useful in metathesis reactions as shown with the synthesis of $Cp_2M(TeSi(SiMe_3)_3)_2$ (M = Ti, Zr).[14] Moreover, the heterobimetallic thiolate $[Cu_4Mes_4]$-$[Mg(SR)_2]_2$ (Mes = $2,4,6$-$Me_3C_6H_2$, SR = $SC_6H_4((R)$-CH-(Me)NMe_2$)), comprising of two magnesium chalcogenolate units bound to a central tetranuclear cuprate moiety, has been related to compounds prepared by Cu-(I)-catalyzed conjugate 1,4-addition of Grignard reagents to enones and other regio- and stereospecific C−C bond-forming processes.[15,16]

Despite the importance of molecular magnesium chalcogenolates in many areas of chemistry, only few compounds have been mentioned in the literature[14-16,22-28] and recently summarized in a review article.[29] The first structurally characterized compound displaying magnesium chalcogenolate interactions was the heteroorganocuprate $[Cu_4Mes_4][Mg(SR)_2]_2$ published in 1990,[15] followed by $Mg(TeSi(SiMe_3)_3)_2(THF)_2$, reported in 1992.[14] The first base-free magnesium chalcogenolate was the dimeric $[Mg(STriph)_2]_2$ (Triph = $2,4,6$-$Ph_3C_6H_2$) published in 1995.[24] The monomeric chalcogenolates $Mg(SMes^*)_2(Et_2O)_2$[24] (Mes* = $2,4,6$-$^tBu_3C_6H_2$), $Mg(SeMes^*)_2(THF)_2$,[24] and $Mg(SeSi(SiMe_3)_3)_2$-(TRMPSI)[28] (TRMPSI = tris((dimethylphosphino)methyl)-*tert*-butylsilane) were reported about the same time, followed by the intramolecularly stabilized dimer $[Mg-\{S(C_6H_4-2-CH_2NMe_2)\}_2]_2$.[25] The common theme among all known magnesium chalcogenolates is the sterically demanding or intramolecularly stabilized chalcogenol employed in their synthesis, which enhances solubility and prevents polymerization. Accordingly, most known target molecules display low coordination numbers.

In this paper, we report the synthesis and characterization of five magnesium thiolates bearing small aromatic ligands. The close chemical and structural relation of the ligands, in conjunction with the strong nitrogen donors pyridine and 2,6-lutidine, have allowed for a detailed analysis of chemical and structural features and their dependence on ligand and donor.

Experimental Section

General Procedures. All reactions were performed under a purified nitrogen atmosphere by using either modified Schlenk techniques or a Braun Labmaster 100 drybox. *n*-Hexane, toluene (tol), tetrahydrofuran (THF), and diethyl ether (Et_2O) were freshly distilled from a Na/K alloy and degassed two times before use. Commercially available $(C_4H_9)_2$-Mg (1.0 M solution in heptane) was used as received. HSPh was stored over dried molecular sieves. HSC_6F_5, pyridine, and 2,6-lutidine were stirred over CaH_2 and distilled. 2-Mercaptopyridine was sublimed prior to use. ^1H (300 MHz) and ^{13}C NMR (100 MHz) spectra were obtained on a Bruker DPX-300 spectrometer. Infrared spectra were recorded as Nujol mulls between KBr plates, using a Perkin-Elmer PE 1600 FT-IR spectrometer. Elemental analyses were excluded because of the high thermal and moisture sensitivity of all compounds reported. For example, typical working time for mounting crystals was less than 10 min before decomposition occurred, even while the crystals were stored under a heavy hydrocarbon oil. In addition, thiolates tend to give notoriously unreliable elemental analyses owing to the formation of nonvolatile metal sulfides.

Synthesis of $Mg(SC_6F_5)_2(py)_3\cdot tol$, 1a, and $Mg(SC_6F_5)_2$-$(py)_3$, 1b. Compounds **1a** and **1b** were synthesized by utilizing

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different stoichiometric amounts of pyridine in the reaction mixture. For compound **1a**, 2 equiv of pyridine/equiv of metal reagent was employed; for compound **1b**, a 3-fold excess of donor (12 mmol) was added to 2 mmol of magnesium reagent. $(C_4H_9)_2Mg$, 2.0 mL (2.0 mmol), was added to 25 mL of toluene in a Schlenk flask. HSC_6F_5, 0.53 mL (4.0 mmol), was added dropwise, resulting in a thick white suspension. This was stirred at room temperature for 10 min, after which excess pyridine (12 mmol) was added at once (compound **1b**) or 2 equiv of pyridine was slowly added via syringe (compound **1a**). The white solid initially dissolved with the addition of pyridine in both reactions, while brief heating was needed to achieve a homogeneous mixture after stirring for 10 min. A pale cloudiness developed on cooling, and the reaction mixtures were further stirred at room temperature for 1 h. Upon being heated to reflux, the solutions again became clear and were filtered while hot through heated Celite-padded frits. Clear, colorless blocks (**1a**) and plates (**1b**) gradually formed as the filtrates cooled to room temperature in 55% (0.69 g) yield (**1a**) and 61% yield (0.80 g) (**1b**). The colorless crystals shrink around 80 °C presumably due to the loss of solvated toluene; the remaining solid decomposes to a brown solid above 150 °C. Compound **1b** decomposes above 150 °C. ^1H NMR and ^{13}C NMR analysis was not possible due to the insolubility of compounds **1a** and **1b** in NMR solvents C_6D_6, THF-d_8, pyridine-d_5, and acetone-d_6. IR (cm^{-1}) (Nujol): 3042 w, 2923 s, 2853 s, 1604 m, 1505 s, 1466 s, 1446 s, 1377 m, 1220 m, 1160 w, 1072 m, 1040 w, 1010 w, 970 s, 860 s, 765 m, 701 s, 630 m, 427 m.

Synthesis of $Mg(SC_6H_5)_2(py)_4$, 2, and $Mg_3(\mu^2\text{-}SC_6H_5)_6$-(py)_6, 3. Both compounds were prepared by similar routes: 0.41 mL (4.0 mmol) HSPh and 25 mL toluene were added to a Schlenk flask, followed by the dropwise addition (syringe) of 2 mL of magnesium reagent $(C_4H_9)_2Mg$ (2 mmol). A thick white slurry quickly formed and was further stirred for 2 h.

For monomeric **2**, a large excess of pyridine (ca. 5 mL) was added until the reaction mixture remained nearly homogeneous at room temperature. Brief heating and filtration through a Celite-padded filter frit led to the formation of clear, plate-shaped crystals at room temperature which were suitable for X-ray crystallography studies. Yield: 80% (0.89 g). In the synthesis of **3**, a smaller amount of pyridine was added dropwise to the reaction mixture (approximately 1.6 mmol), causing the mixture to become homogeneous while hot. The hot solution was filtered through a Celite-padded frit. After storage at room temperature for 1 day, a white powder was observed, which had lightly coated the vessel sides, followed by the formation of colorless block-shaped crystals suitable for X-ray diffraction studies. The combined yield of powder and crystals was 0.60 g (50% yield). Compound **2**: the white powder begins to shrink at 85 °C and then melts reversibly to a clear oil at 96–100 °C. Compound **3**: 120–125 °C.

Compound 2. ^1H NMR (THF-d_8), δ: 8.61 (d, 12 H), 6.85 (m, 12 H), 6.72 (m, 6H). $^{13}C\{^1H\}$ NMR (THF-d_8), δ: 150.83, 137.06, 134.89, 128.00, 124.69, 121.77. IR (cm^{-1}) (Nujol): 3060 w, 2922 s, 2853 s, 1599 m, 1575 m, 1457 m, 1439 m, 1377 m, 1220 m, 1144 w, 1084 m, 1068 m, 1034 m, 1024 m, 998 w, 767 w, 738 s, 713 m, 699 s, 627 w, 617 m, 487 w, 425 m.

Compound 3. ^1H NMR (THF-d_8), δ: 8.63 (m, 12H), 7.71 (m, 6H), 7.42 (d, 12H), 7.29 (m, 12H), 6.86 (t, 12H), 6.73 (t, 6H). $^{13}C\{^1H\}$ (THF-d_8), δ: 150.78, 137.34, 134.92, 128.00, 124.80, 121.80. IR (cm^{-1}) (Nujol): 3054 w, 2927 s, 2854 s, 1601 s, 1572 s, 1471 s, 1443 s, 1377 m, 1214 w, 1151 w, 1083 m, 1039 m, 1007 m, 736 s, 693 s, 625 m, 481 w, 423 s.

Synthesis of $Mg(S\text{-}2\text{-}NC_5H_4)_2(py)_2$, 4. A 100 mL Schlenk flask was charged with 0.22 g (2.0 mmol) of 2-mercaptopyridine and 30 mL of toluene and heated briefly until the solution became homogeneous. $(C_4H_9)_2Mg$, 1.0 mL (1.0 mmol), was added dropwise by syringe, resulting in a pale yellow suspension. After brief heating to reflux temperature, 0.2 mL (2.5 mmol) pyridine was added dropwise, causing the suspension

to become a homogeneous, pale yellow solution. The reaction mixture was filtered at room temperature through a Celite-padded frit. After overnight storage at 0 °C, 0.13 g (32%) of colorless crystals suitable for crystallographic analysis was obtained. Shrinking above 115 °C; reversible melt to a yellow oil, 185–190 °C. ^1H NMR (THF-d_8, δ: 8.63 (b d, 2H), 7.89 (b d, 1H), 7.70 (b t, 1H), 7.29 (b t, 2H), 7.16 (m, 2H), 6.47 (b t, 1H). $^{13}C\{^1H\}$ NMR (THF-d_8), δ: 178.20, 150.79, 146.06, 137.09, 136.80, 128.02, 124.69, 114.92. IR (cm^{-1}) (Nujol): 3051 w, 2916 s, 1585 s, 1484 s, 1439 s, 1441 s, 1262 m, 1220 m, 1183 w, 1133 s, 1084 m, 1070 m, 1037 m, 1005 m, 752 s, 728 m, 698 s, 642 m, 627 m, 486 m, 453 m.

Synthesis of $[C_7H_9NH]_2[Mg(SC_6F_5)_4]$, 5. HSC_6F_5, 0.5 mL (4.0 mmol), was diluted in 30 mL of toluene, followed by the addition of 1.0 mL (1.0 mmol) of $(C_4H_9)_2Mg$. A heavy white precipitate quickly formed. After dropwise addition of 0.2 mL (2.1 mmol) of 2,6-lutidine, the solution momentarily became homogeneous and then developed a yellow cloudiness. The suspension was stirred at room temperature for 1 h, followed by brief heating to reflux temperature, whereupon the solution again became homogeneous and was immediately filtered through a Celite-padded frit. When the sample was allowed to cool to room temperature, a slight haze developed, followed by the gradual formation of colorless needles in 37% yield (0.37 g). Irreversible melt to a yellow oil, 120–123 °C dec. ^1H NMR (THF-d_8), δ: 7.48 (t, 2H), 6.96 (d, 4H), 6.24 (b s, 2H), 2.45 (s, 12H). $^{13}C\{^1H\}$ NMR (THF-d_8), δ: 157.93, 147.29, 146.08, 138.73, 137.99, 121.23, 23.92. IR (cm^{-1}) (Nujol): 3050 w, 2920 s, 2756 s, 1636 s, 1505 s, 1470 s, 1377 s, 1278 w, 1169 w, 1081 m, 969 s, 861 s, 800 m, 721 w, 558 w.

X-ray Crystallographic Studies. X-ray-quality crystals for all compounds were grown as described previously in this section. The crystals were removed from the Schlenk tube under a stream of N_2 and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected under the microscope, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer.[30] Data sets for all compounds, except **1b**, were collected using a Siemens SMART system complete with three-circle goniometer and CCD detector operating at −54 °C. The data collection nominally covered a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different ϕ angle, and each exposure covered 0.3° in ω. The data set for compound **1b** was collected on a Siemens P4 diffractometer equipped with rotating-anode generator. The data sets of compounds **1a** and **3**–**5** were collected at −123 °C using a Cryojet low-temperature device from Oxford Instruments; that for compound **2** was collected at −118 °C using a locally modified Siemens LT-2 low-temperature device. The data for compound **1b** were collected at −147 °C using a locally modified LT-2 low-temperature device. For compounds **1a** and **2**–**5**, graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) was employed; for **1b**, Ni-filtered Cu Kα radiation ($\lambda = 1.541\,78$ Å) was used. Crystal decay was monitored for compounds **1a** and **2**–**5** by repeating a set of initial frames at the end of the data collection and analyzing the duplicate reflections. No decay was observed. For compound **1b**, two check reflections were measured every 198 reflections and showed only statistical variations in intensity (<1.5%). An absorption correction for compounds **1a** and **2**–**5** was applied by utilizing the program SADABS.[31] XABS2[32] was employed for an empirical absorption correction for compound **1b**. Extinction effects were considered for compound **5** but disregarded in all other cases. The crystal structures of all compounds were solved by direct methods as included in the SHELXTL program package.[33]

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Table 1. Summary of Data Collection, Structure Solution, and Refinement Details for Mg(SC$_6$F$_5$)$_2$(py)$_3$·tol, 1a, Mg(SC$_6$F$_5$)$_2$(py)$_3$, 1b, Mg(SPh)$_2$(py)$_4$, 2, Mg$_3$(μ_2-SPh)$_6$(py)$_6$, 3, Mg(S-2-NC$_5$H$_4$)$_2$(py)$_2$, 4, and [C$_7$H$_9$NH]$_2$[Mg(SC$_6$F$_5$)$_4$], 5

	1a	1b	2	3	4	5
formula	C$_{34}$H$_{23}$F$_{10}$MgN$_3$S$_2$	C$_{27}$H$_{15}$F$_{10}$MgN$_3$S$_2$	C$_{32}$H$_{30}$MgN$_4$S$_2$	C$_{66}$H$_{60}$Mg$_3$N$_6$S$_6$	C$_{20}$H$_{18}$MgN$_4$S$_2$	C$_{38}$H$_{20}$F$_{20}$MgN$_2$S$_4$
fw	751.98	659.85	559.03	1202.47	402.81	1037.11
crystal descripn	color/block	color/parallepip	color/plate	color/cube	color/rod	color/needle
crystal size [mm]	0.3 × 0.3 × 0.2	0.5 × 0.1 × 0.05	0.25 × 0.25 × 0.15	0.20 × 0.20 × 0.20	0.20 × 0.30 × 0.09	0.4 × 0.1 × 0.07
a, Å	8.9017(2)	8.958(5)	16.8489(3)	11.6211(6)	30.3965(5)	10.2833(4)
b, Å	12.6760(3)	13.093(11)	8.9070(1)	11.7409(6)	9.6517(2)	13.0697(5)
c, Å	16.0712(4)	13.209(9)	18.6346(4)	12.3730(6)	30.9695(4)	16.7698(2)
α, deg	67.916(1)	67.03(6)	90	102.010(1)	90	105.029(2)
β, deg	84.488(1)	7547(5)	90.528(1)	105.674(1)	116.209(1)	102.624(2)
γ, deg	81.093(1)	80.28(6)	90	94.666(1)	90	104.037(2)
V, Å^3	1658.71(7)	1377(2)	2796.43(8)	1572.79(14)	8151.6(2)	2014.24(11)
Z	2	2	4	1	16	2
space group	$P\bar{1}$	$P\bar{1}$	I_2/a	$P\bar{1}$	I_2/a	$P\bar{1}$
d_{calc}, g/cm^3	1.506	1.592	1.328	1.270	1.313	1.707
lin abs coeff mm^{-1}	0.266	0.283	0.242	0.293	0.304	0.378
radiation	Mo Kα	Cu Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
T, K	150	126	155	150	150	150
2θ range deg	3−50	7−110	4−57	3−50	0−57	2−57
no. of indep reflns	5440	3461	3408	5243	9403	8314
no. of params	451	388	178	430	567	595
R1, wR2 (all data)^a	0.1174, 0.1928	0.1228, 0.2574	0.0711, 0.1002	0.1006, 0.1796	0.1631, 0.2009	0.2557, 0.1835
R1, wR2 (>2σ)^a	0.0765, 0.1694	0.0838, 0.2084	0.0462, 0.0873	0.0673, 0.1595	0.1092, 0.1798	0.0895, 0.1341

^{a} R1 = $\sum ||F_o| - |F_c||/\sum |F_o|$; wR2 = $\{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$.

Missing atoms were located in subsequent difference Fourier cycles and included in the refinement. The structures of all compounds were refined by full-matrix least-squares refinement on F^2 (SHELX-93).[34] Hydrogen atoms were placed geometrically and refined using a riding model, including free rotation about C−C bonds for methyl groups. For all compounds, hydrogen atoms were refined with U_{iso} constrained at 1.2 (for non-methyl groups) and 1.5 (for methyl groups) times U_{eq} of the carrier C atom. The hydrogen atoms on the protonated 2,6-lutidine in compound **5** were located in a difference Fourier map and included in the refinement. Their positional and thermal parameters were included as free variables. The crystallographic programs used for structure refinement and solution were installed on either a PC clone or a Silicon Graphics Indigo^2 R10000 Solid Impact. Scattering factors were those provided with the SHELX program system.[34] All non-hydrogen atoms, with the exception of those in some disordered or restrained positions, were refined anisotropically. Disorder was typically handled by introducing split positions for the affected groups into the refinement of the respective occupancies. Generally, a set of restraints was applied to aid in modeling the disorder.[34] Disorder was especially severe in the case of compound **4**, where the 2-mercaptopyridine ligands and pyridine donors were observed to exchange positions in the crystal, resulting in overlaid ligand and donor functions. This disorder was handled by defining independent ligand and donor positions and refinement of the respective occupancies. Table 1 summarizes pertinent details of the data collections and structure refinements, while Table 2 lists important geometrical data for compounds **1**−**5**. Further details regarding the data collections, structure solutions, refinements, and how disorder was handled are outlined in the Supporting Information.

Results and Discussion

Structural Descriptions. **Mg(SC$_6$F$_5$)$_2$(py)$_3$·tol, 1a, and Mg(SC$_6$F$_5$)$_2$(py)$_3$, 1b.** Compounds **1a** and **1b**

display very similar structural features for the main molecule, which is depicted in Figure 1. Important crystallographic data are summarized in Table 1, and selected geometrical parameters are listed in Table 2. Compounds **1a** and **1b** can be described as monomeric neutral units with no crystallographically imposed symmetry. Magnesium is surrounded in a severely distorted trigonal bipyramidal manner by two pentafluorobenzenethiolate groups and three pyridine donors, with the bulkier SC$_6$F$_5$ ligands in the equatorial plane and the smaller pyridine donors in one equatorial and the axial positions. The S−Mg−S angles are 138.78(8)° (**1a**) and 136.4(1)° (**1b**); the equatorial N−Mg−S angles are found at 82.2(1) and 94.1(1)° (**1a**) and 83.1(2) and 91.6(2)° (**1b**). The distortion in the equatorial plane also affects the axial geometry: the axial pyridine groups bend toward the equatorial plane, with N(1)−Mg−N(3) angles of 168.0(2)° (**1a**) and 168.6(3)° (**1b**). The magnesium−sulfur distances are observed at 2.470(2) and 2.481(2) Å (**1a**) and 2.476(4) and 2.505(4) Å (**1b**), with Mg−S−C angles at 109.5(2) and 111.4(2)° (**1a**) and 109.9(3) and 110.2(3)° (**1b**). The Mg−N distances lie in narrow ranges between 2.136(4) and 2.210(4) Å (**1a**) and between 2.139(7) and 2.191(6) Å (**1b**). The S−C distances are observed at 1.75(1) Å (average) (**1a**) and 1.76(1) Å (average) (**1b**). Overall, the structural differences between compounds **1a** and **1b** are only marginal, taking into account that their intensity data sets were collected at different temperatures (−123 °C for **1a** and −147 °C for **1b**).

Mg(SC$_6$H$_5$)$_2$(py)$_4$, 2. Compound **2**, shown in Figure 2, crystallizes as a neutral monomeric species. The magnesium center is surrounded in an octahedral fashion by two SPh ligands and four pyridine donors. A center of symmetry is located at magnesium, resulting in one independent thiolato and two independent pyridine functions. The two thiolate groups are located

(33) Sheldrick, G. M. SHELXL-76: Program for crystal structure refinement. University of Göttingen, Germany, 1976.

(34) Sheldrick, G. M. SHELXL-93: Program for crystal structure refinement. University of Göttingen, Germany, 1993.

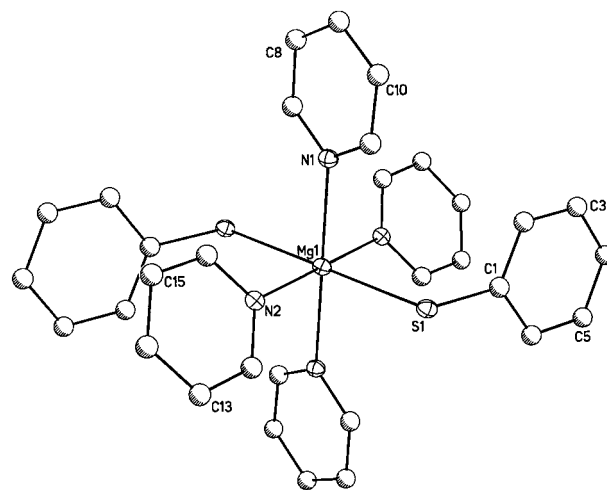**Table 2.   Important Bond Lengths and Angles in Compounds 1−5 and Related Magnesium Thiolates**[a]

compound	Mg–S, Å	Mg–donor, Å	S–C$_{ipso}$, Å	Mg–S–C, deg	CN	ref
[Mg(STriph)$_2$]$_2$	2.466(5)$_{br}$, 2.458(5)$_{br}$, 2.349(5)$_t$	2.555,[b] 2.797[b]	1.775(6)	91.3(4), 122.1(4)	3 (+2)	24
Mg(SMes*)$_2$(Et$_2$O)$_2$	2.382(2), 2.392(2)	2.074(3),[c] 2.065(3)[c]	1.798(4), 1.807(4)	116.6(1), 117.1(1)	4	24
Mg(SSiPh$_3$)$_2$(HMPA)$_2$	2.431(2), 2.430(2)	1.942(3),[e] 1.945(3)[e]	2.073(2),[g] 2.079(2)[g]	112.24(7), 116.56(8)	4	40
[(C$_7$H$_9$NH)]$_2$ [Mg(SC$_6$F$_5$)$_4$], **5**	2.416(3), 2.464(3), 2.432(3), 2.483(3)		1.753(7), 1.756(7), 1.751(8), 1.757(6)	102.4(2), 105.0(2), 106.6(2), 108.7(2)	4	h
Mg(SC$_6$F$_5$)$_2$(py)$_3$·tol, **1a**	2.470(2), 2.481(2)	2.136(4),[d] 2.210(4,[d] 2.202(4)[d]	1.753(5), 1.754(5)	109.5(2), 111.4(2)	5	h
Mg(SC$_6$F$_5$)$_2$(py)$_2$, **1b**	2.476(4), 2.505(4)	2.139(7),[d] 2.184(6),[d] 2.191(6)[d]	1.752(8), 1.757(7)	109.9(3), 110.2(3)	5	h
[Mg(SC$_6$H$_4$-2-CH$_2$NMe$_2$)$_2$]$_2$	2.519(2)$_{br}$,, 2.578(2)$_{br}$, 2.446(2)$_t$	2.252(3),[d] 2.239(4)[d]	1.761(4), 1.770(4)	94.2(1), 104.11(5), 108.2(1)	5	25
Mg(SPh)$_2$(py)$_4$, **2**	2.6247(5)	2.220(2),[d] 2.360(2)[d]	1.771(2)	108.95(6)	6	h
Mg(S-2-NC$_5$H$_4$)$_2$(py)$_2$, **4**	2.612(2), 2.613(2), 2.589(5), 2.604(6), 2.626(2), 2.659(2)	2.149(3),[d] 2.165(3),[d] 2.186(5),[d] 2.188(6),[d] 2.194(5),[d] 2.200(6),[d] 2.213(3),[d] 2.246(3)[d]	1.763(3), 1.748(3)	76.3(1), 77.33(12), 77.4(2), 76.33(13), 76.9(6), 80.6(3)	6	h
Mg$_3$(μ_2-SPh)$_6$(py)$_6$, **3**	2.5799(9), 2.596(2), 2.6140(14), 2.628(2), 2.6579(9), 2.6720(9)	2.202(3),[d] 2.232(3),[d] 2.233(3)[d]	1.773(2), 1.771(3), 1.781(3)	82.44(4), 83.34(4), 84.52(4), 109.4(1), 109.6(2), 117.0(2), 118.47(8), 118.83(9), 120.8(2), 124.41(8)	6	h
Mg(15-crown-5)(SCP$_3$)$_2$	2.660(1)	2.150(2), 2.182(1), 2.190(2), 2.194(2), 2.194(2)	1.865(2)	124.99(6)	7	40
[Mg(15-crown-5)(THF)$_2$] [SMes*]$_2$		2.088(3),[c] 2.098(3),[c] 2.118(4),[f] 2.160(4),[f] 2.172(4),[f] 2.189(4),[f] 2.195(4)[f]	1.766(5), 1.779(5)		7	40

[a] Abreviations: Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$, Triph = 2,4,6-Ph$_3$C$_6$H$_2$, py = pyridine, Mes = 2,4,6-Me$_3$C$_6$H$_2$, Ar = C$_6$H$_4$(CHMeNMe$_2$), t = terminal, br = bridging. [b] Magnesium−carbon contact. [c] Mg−THF/Et$_2$O contacts. [d] Magnesium−nitrogen contact. [e] Magnesium−oxygen HMPA contact. [f] Mg−crown ether contacts. [g] Sulfur−silicon contact. [h] This work.
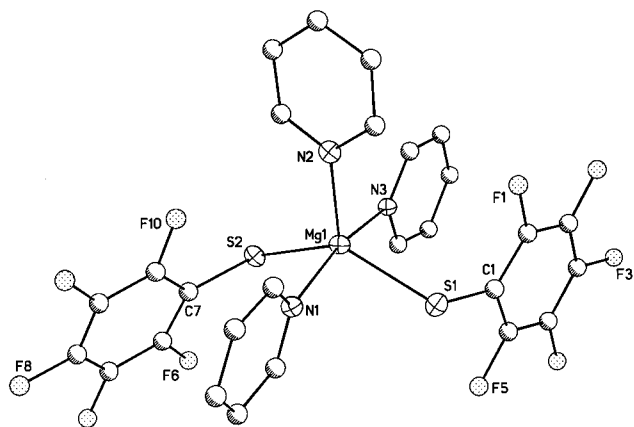
Figure 1. Computer-generated plot of **1**. Hydrogen atoms have been omitted for clarity.

Figure 2. Computer-generated plot of **2**. Hydrogen atoms have been omitted for clarity.
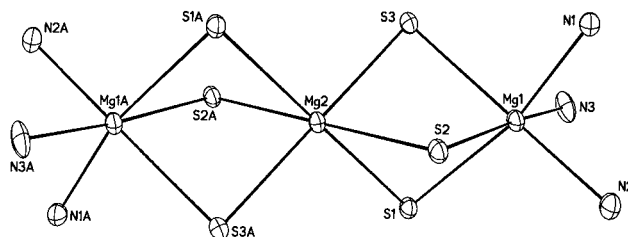
Figure 3. Computer-generated plot showing the framework of **3**. Carbon and hydrogen atoms have been omitted for clarity.

trans to one another; the Mg−S distance is displayed at 2.6247(5) Å. The S−C contact is observed at 1.771-(2) Å with an Mg−S−C angle of 108.95(6)°. The two Mg−N bond lengths are significantly different at 2.220-(2) and 2.360(2) Å.

[Mg$_3$(μ^2-SPh)$_6$(py)$_6$], 3. Compound **3**, the framework of which is depicted in Figure 3, exhibits a trimeric structure with an inversion center located at the central magnesium atom. Figure 4 features a view of the entire molecule. Each asymmetric unit contains half of a trimer. Positional disorder of some of the thiolate and pyridine groups was observed and handled by introduction of split positions and refinement of the respective occupancies. All magnesium centers are six-coordinate with almost undisturbed octahedral geometry: the angles about the magnesiums are about 90 and 180°. The central magnesium unit is ligated to six bridging sulfur atoms, with magnesium−sulfur distances between 2.5799(9) and 2.6720(9) Å. The S−C distances are observed at 1.771(3), 1.773(2), and 1.781(3) Å. The

bridging Mg−S−Mg angles are relatively narrow at 82.44(4), 83.34(4), and 84.52(4)°. The two identical outer magnesium atoms are linked to the central magnesium atom via three bridging thiolato functions. Each of the outer magnesium atoms is also ligated by three terminal pyridine donors, resulting in an overall
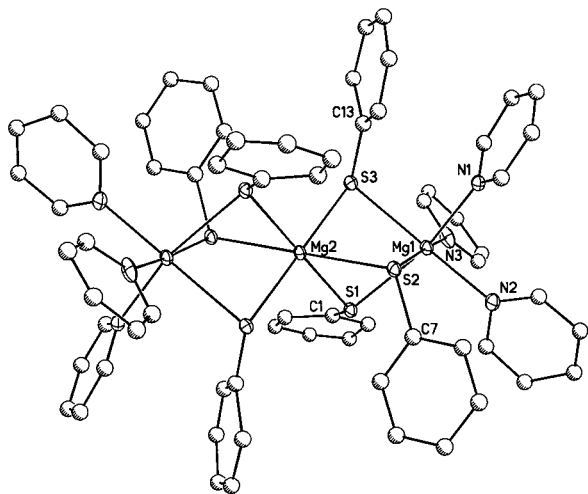
Figure 4. Computer-generated plot of **3**. Disordered positions and hydrogen atoms have been omitted for clarity.
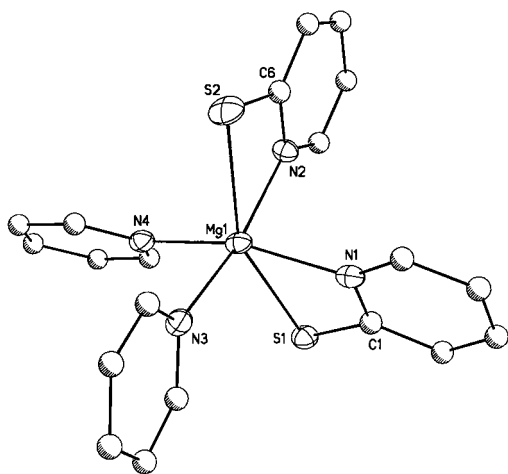
Figure 5. Computer-generated plot of **4**. Disordered positions and hydrogen atoms have been omitted for clarity.

ligand:donor stoichiometry of 1:1. The Mg−N contacts are found at 2.202(3), 2.232(3), and 2.233(3) Å. The trimer can also be described as three face-sharing octahedrons.

Mg(S-2-NC₅H₄)₂(py)₂, 4. Compound **4**, shown in Figure 5, crystallizes with two independent molecules in each asymmetric unit, both of which display fairly similar structural parameters. Severe positional disorder between the 2-mercaptopyridine ligands and the pyridine donors made necessary the introduction of split parameters, resulting in a complicated refinement model. The magnesium atoms are bound to two thiolate sulfur atoms and four nitrogen donors, two from the intramolecular coordinating 2-mercaptopyridine ligand and two from pyridine donors. The intramolecular coordination of the 2-mercaptopyridine ligand results in severe distortion from regular octahedral geometry. Accordingly, the S−Mg−S angles are observed at 154.46-(9) and 156.2(3)°, while selected N−Mg−N angles are found at 166.1(3), 165.9(1), and 160.4(1)°. The magnesium−sulfur distances are observed between 2.612(2) and 2.659(2) Å, and S−C distances are exhibited between 1.748(3) and 1.763(3) Å. The Mg−N contacts within the intramolecuraly coordinating ligand are observed between 2.149(3) and 2.246(3) Å. The Mg−N contacts for the pyridine are found at 2.173(3), 2.227-
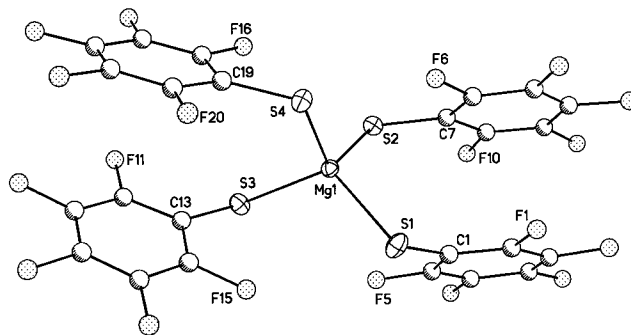
Figure 6. Computer-generated plot of **5**. Only the anion [Mg(SC₆F₅)₄]²⁻ is shown.

(3), 2.188(6), and 2.200(6) Å, while the S−Mg−N angles in the intramolecuraly coordinating ligand are quite acute at 64.59(10), 65.19(9), 65.39(11), and 66.42(10)°.

[C₇H₉NH]₂ [Mg(SC₆F₅)₄], 5. Compound **5**, the anion of which is depicted in Figure 6, consists of separated anions and cations with no crystallographically imposed symmetry. Each asymmetric unit contains one anion and two cations. The cations are protonated 2,6-lutidine molecules, the N−H protons of which have been located in a difference Fourier map and included in subsequent refinement cycles. Weak interactions are observed between the NH function on the cation and neighboring sulfur and fluorine atoms on the anion with H(1A)−F(20) 2.431 Å, H(1A)−S(4) 2.208 Å, H(2A)−F(11) 2.815 Å, and H(2A) − S(3) 2.350 Å. All other intermolecular contacts are above 3.5 Å. The anion displays a distorted tetrahedral magnesium center surrounded by four thiolate ligands. The deviation from regular tetrahedral geometry is made evident by the variation of the S−Mg−S angles, ranging from 97.1(1) to 120.2(1)°. The magnesium−sulfur distances fall in a fairly narrow range and are observed between 2.416(3) and 2.483(3) Å. The S−C contacts are found between 1.751(8) and 1.757(6) Å, with Mg−S−C angles at 102.4(2), 105.0(2), 106.6(2), and 108.7(2)°.

Discussion

Compounds **1**−**4** were synthesized in a straightforward manner by an alkane elimination reaction involving the treatment of $(C_4H_9)_2Mg$ with arenethiolates under addition of pyridine:

$$m(C_4H_9)_2Mg + 2mHSR + n \, \text{donor} \rightarrow$$
$$[Mg(SR)_2(\text{donor})_n]_m + 2mC_4H_{10} \quad (2)$$

$m = 1, 3; \, R = C_6H_5, C_6F_5, 2\text{-}NC_5H_4;$
$$n = 2, 3, 4; \, \text{donor} = \text{pyridine}$$
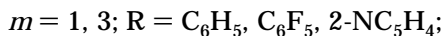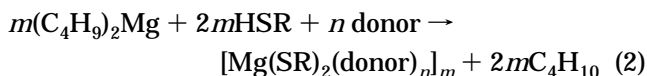
Compound **5** was initially prepared by a similar reaction route in low yields but can be prepared in a rational manner by treating $(C_4H_9)_2Mg$ with 4 equivalents of HSC_6F_5 under addition of 2,6-lutidine:

$$(C_4H_9)_2Mg + 4HSC_6F_5 + 2(2,6\text{-}Me_2NC_5H_4) \rightarrow$$
$$[2,6\text{-}Me_2NHC_5H_4]_2[Mg(SSC_6F_5)_4] + 2C_4H_{10} \quad (3)$$
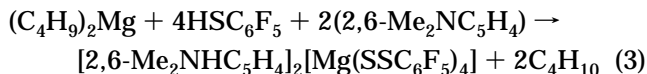
The reaction of dibutylmagnesium with chalcogenol has been used extensively for the synthesis of magnesium chalcogenolates bearing a wide variety of ligands and donors.[14,24,28,29] The products are generally isolated

in excellent yield and purity, indicating the high synthetic potential of this reaction scheme. The reaction proceeds cleanly within a short time, and purification steps are simple or can be avoided due to the gaseous nature of the byproducts. Noticeable is a reduced solubility of the target compounds as compared to known magnesium thiolates bearing sterically demanding ligands. Generally, a strong donor such as pyridine is needed to improve solubility.

In contrast to the wealth of information for magnesium alkoxy, aryloxy, siloxy, and related species,[35] only a handful of complexes involving the heavier chalcogen elements have been described, resulting in a rather limited tableau of structural diversity. Compounds **1**−**5** have been prepared using small arenethiols in conjunction with strong nitrogen donors and therefore add new structural principles to the short list. This results in an improved understanding of ligand and donor effects on the structural chemistry of the target molecules and allows for the rational design of optimized magnesium chalcogenolate precursors and reagents.

The predominant coordination geometry about the Mg^{2+} cation has been found to be either tetrahedral or octahedral. For example, recent gas-phase experimental work has indicated a stable $[Mg(THF)_4]^{2+}$ core as the basis of numerous octahedral complexes.[36] Another report, describing an extensive search of magnesium-containing structures in the Cambridge Structural Database,[37] coupled with ab initio molecular studies, has identified the octahedral species $[Mg(OH_2)_6]^{2+}$ as the most stable in aqueous solution.[38] Known examples of magnesium thiolates generally display the low coordination numbers 2−5. Recently, a presumably monomeric two-coordinate species $Mg(S-2,6-Mes_2C_6H_2)_2$ was reported, but no structural evidence supports this assumption.[39] Other examples include the dimeric [Mg-$(STriph)_2]_2$, exhibiting a magnesium center bound to three thiolato sulfur atoms. Additional metal stabilization is provided by three arene interactions with the ortho phenyl groups of the ligand.[24] Four-coordinate magnesium thiolates include the neutral derivatives $Mg(SMes^*)_2(OEt_2)_2$,[24] and $Mg(SSiPh_3)_2(HMPA)_2$[40] (HMPA = hexamethylphosphortriamide) and the bimetallic aggregate $[Mg_2(SC_6H_4((R)-CH(Me)NMe_2))_4Cu_4(Mes)_4]$.[15] A single example of a five coordinate magnesium thiolate exists: the intramolecular stabilized species $[Mg(SC_6H_4-2-CH_2NMe_2)_2]_2$ described recently.[25] In this paper, we present a family of neutral magnesium thiolates exhibiting coordination numbers 5 and the previously unknown 6, as well as the first magnesiate thiolate.

Monomeric $Mg(SC_6F_5)_2(py)_3$, **1**, available by treatment of $(C_4H_9)_2Mg$ with the perfluorinated ligand HSC_6F_5 and pyridine in good yield, displays a distorted five coordinate magnesium center which is linked to three nitrogen donors and two thiolato sulfur atoms (Figure 1). The distorted trigonal bipyramidal geometry can be rationalized by invoking VSEPR rules,[41] assuming a distortion from trigonal bipyramidal geometry with the bulkier SC_6F_5 ligands in the equatorial plane and the smaller pyridine donors in the remaining equatorial and the two axial positions. The two neighboring fluorinated thiolate ligands repel each other, resulting in a widening of the S−Mg−S angle to 136.4(1)° (**1b**) or 138.78(8)° (**1a**), respectively. Simultaneously, the pyridine groups will distort from the axial positions toward the equatorial plane, resulting in an N(1)−Mg-N(3) angle of 168.0(2)° (**1a**) or 168.6(3)° (**1b**). In contrast, the analogous reaction utilizing HSC_6H_5 and a large excess of pyridine results in the formation of the octahedral complex Mg-$(SPh)_2(py)_4$, **2** (Figure 2). In this six-coordinate monomer, the environment about the cation is now occupied by four pyridine molecules as well as two benzenethiolate ligands.

Reducing the steric presence from HSC_6F_5 to HSC_6H_5 facilitated the coordination of four pyridine donors in **2** in contrast to three in **1**. Coupled with an increase in coordination number is an increase in bond lengths, which is reflected in both the Mg−S [2.476(4) and 2.505-(4) Å for **1** and 2.6247(5) Å for **2**] and Mg−N distances [2.139(7), 2.184(6), and 2.191(6) in **1** and 2.360(2) and 2.220(2) Å in **2**]. The reduced steric presence of the benzenethiolate, however, does not allow for equal pyridine coordination in **2**, as exemplified by the significantly different Mg−N contacts: two donors interact with the metal at 2.220(2) Å, while the remaining two ligands cannot approach as close at 2.360(2) Å, a difference of 0.140 Å.

The magnesium−sulfur distances in **1** may be compared with those in the five-coordinate $[Mg(SC_6H_4-2-CH_2NMe_2)_2]_2$.[25] Here, each magnesium atom is ligated by three sulfur atoms, with two bridging [2.548(2) Å average] and one terminal Mg−S [2.446(2) Å] contacts. Very similar Mg−S distances are also observed in the five-coordinate anion $[Mg(NH_3)_2(SC_6H_5)_3]^-$ (2.524(2) Å).[42] The comparison of magnesium−sulfur bond lengths for the five- and six-coordinate thiolates **1** and **2** with the sum of ionic radii for five or six coordinate Mg^{2+} and S^{2-} results in very comparable values (2.50 and 2.56 Å),[43] supporting the view of a mainly ionic interaction between the metal center and the ligand. This is further supported by ab initio calculations by Pappas, who described the Mg−S interactions as predominantly ionic. Pappas also calculated the Mg−S bond length in a hypothetical, two-coordinate $Mg(SH)_2$ to be 2.324 Å, a value significantly shorter than that observed for **1** and **2**.[44] The deviations in bond lengths can be clearly accredited to the differences in coordination numbers.

The magnesium−nitrogen contacts in **1** and **2** are also very comparable to those in other five- and six-coordinate magnesium complexes such as the five-

(35) See, for example: (a) Calabrese, J.; Cushing, M. A.; Ittel, S. D. *Inorg. Chem.* **1988**, *27*, 867. (b) Kostas, I.; Screttas, C. G. *J. Org. Chem.* **1997**, *62*, 5575. (c) Screttas, C. G.; Steele, B. R. *J. Org. Chem.* **1989**, *54*, 1013. (d) Kaomata, N.; Nakata, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1207. (e) Tinoco, I.; Kieft, J. S. *Nature, Struct. Biol.* **1997**, *4*, 509. (f) Yun, J. W.; Tanase, T.; Lippard, S. J. *Inorg. Chem.* **1996**, *35*, 7590. (g) *The Biological Chemistry of Magnesium*; Cowan, J. A., Ed.; VCH: New York, 1995.
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coordinate dimer $[Mg(SC_6H_4-2-CH_2NMe_2)_2]_2$ [2.239(4) and 2.252(3) Å],[25] the anion $[Mg(NH_3)_2(SC_6H_5)_3]^-$ [2.20-(1) Å],[42] or the five-coordinate trimer [Mg(1,8-diami-donaphthalene)(HMPA)]$_3$ [2.16(2) Å].[45] As expected, Mg−N bond lengths increase as the coordination number increases, as observed in **2** and the six-coordinate cation $[Mg(NH_3)_6]^{2+}$ [2.21(1) Å average].[42] The relatively short Mg−N bond lengths in the latter can be explained by the cationic charge, as evidenced by the close similarity between the Mg−N distances in the five-coordinate anion $[Mg(NH_3)_2(SC_6H_5)_3]^-$ [2.20(1) Å] and the six-coordinate cation $Mg(NH_3)_6]^{2+}$ [2.21(1) Å].[42] The short Mg−N distance [2.220(2) Å] in **2** agrees well with other experimental values, whereas the weaker, longer bond [2.360(2) Å] differs significantly. A comparison of **2** with the isostructural complexes $[Yb(EPh)_2(py)_4]$ (E = S, Se)[46] and $Ca(SC_6F_5)_2(py)_4$[47] shows uniform metal−nitrogen contacts in the latter, suggesting that the two short and the two long Mg−N contacts in **2** are the consequence of steric crowding about the small magnesium center. Both calcium (1.14 Å) and ytterbium (1.16 Å) possess significantly larger ionic radii than magnesium (0.86 Å),[43] enabling the ligation of two thiolate ligands in addition to four pyridine donors.

Addressing further the steric crowding at magnesium in compound **2**, a reduced amount of pyridine was utilized in a subsequent reaction with the intention of synthesizing a species with fewer pyridine donors bound to magnesium. To our surprise, the trimeric $[Mg_3(\mu_2$-SPh)$_6$(py)$_6]$, **3** (Figures 3 and 4), and not the monomeric five-coordinate $Mg(SPh)_2(py)_3$, as expected from previous results with HSC_6F_5, was reproducibly isolated in good yield and purity. Apparently, the steric bulk of SPh is not sufficient to stabilize a five-coordinate metal center. Compound **3** exhibits octahedrally coordinate metal centers: the central magnesium unit is bound to six bridging thiolate sulfur atoms, while the two outer magnesium atoms are connected to three bridging sulfur atoms in addition to three terminal pyridine molecules, resulting in a ligand:donor stoichiometry of 1:1. Compound **3** is a rare example of a main group chalcogenolate in which octahedrons are connected via shared faces. Commonly, metal complexes are connected via edges or vertexes, as seen in the dimeric $[Mg(SC_6H_4-2-CH_2NMe_2)_2]_2$[25] or in $[Mg\{Nb(OEt)_6\}_2]$,[48] featuring a central four-coordinate magnesium cation linking two octahedral niobium hexaethoxide anions. A rare example in which face sharing is observed is $[M(M'-(O^tBu)_3)_2]$ (M = Mg, Ca, Sr, Ba; M' = Ge, Sn, Pb), where octahedrally coordinate alkaline-earth cations tether two M'(II) tris(*tert*-butyloxo)metalates.[49,50] Few other examples have been reported for transition metal derivatives; among those, dinuclear species are most often observed, and trinuclear complexes are more rare. Some examples of dinuclear thiolate complexes with a

face-sharing motif include the titanium compound $[NMe_2H_2][Ti_2(SMe)_9]$,[51] the dinuclear cobalt derivatives $[NMe_4][Co_2(SC_3H_7)_5]$[52] and $[Li(OEt_2)_3][Co_2(S2,4,6-^iPr_3C_6H_2)_5]$,[53] and the dinuclear $[NMe_4][Fe_2(SC_4H_9)_5]$.[54] An example of a trinuclear derivative is the titanium species $Ti_3(SMe)_{12}$.[51]

The Mg−S contacts in the six-coordinate **3** are found in the range 2.580(1)−2.672(1) Å, while Mg− N bonds are exhibited between 2.202(3) and 2.233(3) Å. These values agree well with those in **2**, indicating the close dependence of bond lengths on coordination number. Compound **3** displays related features with the titanium trimer, $Ti_3(SMe)_{12}$, with the exception that the pyridine donors in **3** are replaced by thiolato groups to accommodate titanium in oxidation state IV.[51]

The synthetic access routes for compounds **2** and **3** are very similar and depend only on the amount of pyridine added: **2** becomes available if a large excess is used; a reduced amount of pyridine results in the formation of **3**. Since compounds **2** and **3** can be interconverted by addition or removal of donor, they must be related by an equilibrium. Compounds **2** and **3** display a rare example where the compounds on both sides of an equilibrium have been structurally characterized in the solid state.

$$3Mg(SPh)_2(py)_4 \leftrightarrow Mg_3(\mu_2\text{-}SPh)_6(py)_6 + 6py \quad (4)$$
$$\mathbf{2} \qquad\qquad\qquad \mathbf{3}$$

Upon analysis of the combined steric effects of ligands and donors in compounds **2** and **3** to obtain further clues regarding the steric crowding in **2**, it became obvious that the replacement of just one pyridine donor by one thiolate ligand, as observed for the outer magnesium atoms in **3**, does relieve steric crowding about the magnesium center, as evidenced by the Mg−N distances in **3**, which range in the narrow margin from 2.202(3) to 2.233(3) Å.

To further evaluate the coordination environment in six-coordinate magnesium thiolates, the conformationally related $Mg(S-2-NC_5H_4)_2(py)_2$, **4** (Figure 5), was prepared. The intramolecular coordinating ligand S-2-NC_5H_4 contributes a thiolate and a nitrogen binding site while exhibiting a significantly reduced steric presence as compared to a single arenethiolate and a pyridine donor. Compound **4**, available by treatment of $(C_4H_9)_2$-Mg with 2 equiv of 2-mercaptopyridine under addition of pyridine, displays a distorted octahedral coordination sphere with magnesium linked to two intramolecular stabilizing 2-mercaptopyridine ligands in addition to two pyridine donors. The intramolecularly stabilizing ligands display a narrow bite angle as indicated by the acute S−Mg−N angles observed in the range 64.59(10)−66.42-(10)°. The intramolecular nature of the ligands results in a distorted octahedral environment with S−Mg−S angles between 154.46(9) and 156.54(9)°, whereas, in **2** or **3**, almost undistorted octahedral geometry at magnesium is observed.

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The comparison of Mg−S distances in the six-coordinate species **2**−**4** reveals comparable numbers: 2.6247(5) Å for Mg(SPh)$_2$(py)$_4$, **2**, an average of 2.612-(2) Å for the trimer **3**, and 2.612(1) Å (average) for Mg-(S-2-NC$_5$H$_4$)$_2$(py)$_2$, **4**. Interestingly, the intramolecularly stabilized **4** does not display shorter Mg−S bonds, as one might expect from its reduced steric bulk. This may be explained by the bidentate nature of the ligand and the acute S−Mg−N angle. The slightly elongated Mg−S bond length in **2**, as compared to **3** and **4**, supports the view of steric crowding about the magnesium center in **2**, as discussed earlier in terms of the asymmetric Mg−N coordination. Striking is also the similarity of Mg−S bond lengths in the monomer **4** and the trimer **3**: the bridging nature of the thiolato groups in **3**, which increases the coordination number at sulfur from 2 to 3, does not result in an increase of Mg−S bond lengths. The three bridging thiolate groups on each side of the metal are arranged in a tightly linked face-sharing octahedral arrangement, resulting in an overall shortening of magnesium−sulfur distances. A similar trend was observed for the Co−S bond lengths in the dimer [Li(OEt$_2$)$_3$][Co$_2$(S-2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_5$],[53] [2.33(2) Å average], where two cobalt atoms are connected via three bridging thiolate groups, as compared to the monomer Co(S-2,6-^{i}Pr$_3$C$_6$H$_3$)$_2$(bpy)(CH$_3$CN)[55] (bpy = bipyridyl) [2.28(2) Å average]. Even shorter Co−S bridging distances were observed in the binuclear [Co$_2$(SC$_3$H$_7$)$_5$]$^-$ anion [2.31(1) Å].[52] In contrast, the dinuclear calcium alkoxide [Ca$_2$(OC^{t}Bu)(CH$_2$O^{i}Pr)$_2$)$_4$], where the cations are bridged via two anionic oxygen atoms and a third neutral donor, displays the expected variation in Ca−O bridging and terminal bond distances of about 0.15 Å.[56] Similar bond length differences were detected in [Ca$_2$(OSiPh$_3$)$_4$(NH$_3$)$_4$],[57] where the dinuclear core is bridged by three oxyanions displaying considerably longer Ca−O distances than the terminal interactions.

To further evaluate the coordination environment of magnesium thiolates, a larger nitrogen donor 2,6-Me$_2$-py (2,6-lutidine) was used in conjunction with HSC$_6$F$_5$. To our surprise, the reaction of (C$_4$H$_9$)$_2$Mg with 2 equiv of HSC$_6$F$_5$ in the presence of 2,6-lutidine yielded the magnesiate thiolate [C$_7$H$_9$NH]$_2$[Mg(SC$_6$F$_5$)$_4$], **5** (Figure 6). Excess acidic thiol must have reacted with the amine base, leading to the observed metalate. Protonation of amine donors has been observed previously in [Me$_2$(H)NCH$_2$CH$_2$C(H)Me$_2$][Pd(SC$_6$F$_5$)$_4$], where HSC$_6$F$_5$ was observed to protonate TMEDA (TMEDA = *N,N,N,N*-tetramethylethylenediamine).[58] Compound **5** can be synthesized in a rational fashion by treating (C$_4$H$_9$)$_2$Mg with 4 equiv of thiol in the presence of 2,6-lutidine. Anionic complexes of the alkaline-earth metals are rare and are generally favored if ligands with low Lewis basicity are connected to the metal center. The Lewis acidic metal center will interact with an increased number of ligands to compensate for its electron deficiency.[59] Magnesiate chalcogenolates are rare; an ex-

ample is the monoprotonated 1,8-bis(dimethylamino)-naphthalene tris(hexafluoroacetylacatonato) magnesiate.[60] Organometallic magnesiates are more common and have been initially described by Wittig.[61] Some examples include the anions [Mg(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_3$]$^-$,[62] [Me$_2$Mg(μ_2-Me)$_2$Mg]$^{2-}$,[63] [MgPh$_4$]$^{2-}$,[64] [MgMe$_4$]$^{2-}$,[64] [Mg(CC^{t}Bu)$_3$]$^-$,[64] [Mg$_2$Et$_6$]$^{2-}$,[65] [MgNp$_3$]$^-$,[65] (Np = neopentyl), and [Mg$_2$Me$_5$]$^-$.[66] Also related to **5** is a zincate complex, [Me$_4$N]$_2$[Zn(SPh)$_4$], where four thiophenolate anions surround the cation in a distorted tetrahedral fashion.[67,68] Monoanionic zinc and cadmium thiolates have also been reported; here three thiolates surround the metal center, while the charge is balanced by either a tetraphenylphosphonium or a tetrapropylammonium cation.[69-71]

Compound **5** consists of protonated 2,6-lutidine cations and tetrakis(thiolato)magnesate anions. The anions display a distorted tetrahedrally coordinate metal center, where magnesium is ligated by four thiolate groups with S−Mg−S angles in the range 97.1(1)−120.2(1)°. The magnesium−sulfur distances in compound **5** are observed between 2.416(3) and 2.483(3) Å. These values are slightly elongated in comparison with those of neutral four-coordinate magnesium thiolates such as the etherate Mg(SMes*)$_2$(OEt$_2$)$_2$ [2.39(1) Å average] or the heteroorganocuprate [Mg$_2$(SC$_6$H$_4$((*R*)-CH(Me)NMe$_2$))$_4$Cu$_4$(Mes)$_4$] [2.375(4) and 2.427(4) Å].[15,16,24] It is believed that the Mg−S bond elongation is due to the anionic nature of the complex. Weak intermolecular interactions are observed between the cationic NH protons and sulfur and fluorine atoms in the ligands. Supporting the view of only weak hydrogen bonding is that the H−S interactions (2.208 and 2.350 Å) are shorter than the corresponding H−F contacts (2.431 and 2.815 Å).

Conclusions

This paper presents a collection of magnesium thiolates, where the use of small arenethiolates resulted in a variety of novel, unusual geometrical principles. Structural motifs include the first six-coordinate magnesium thiolates, one of which displays a rare face-sharing connectivity, in addition to the first magnesiate thiolate.

The stepwise reagent modification in the synthetic procedures allowed the in depth analysis of structural principles with regard to donor and ligand and resulted

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in an improved understanding of aggregation and association patterns governing magnesium chalcogenolate chemistry. The close connection of structural parameters and physical properties in this family of compounds is evidenced by the comparison of melting points for the various magnesium thiolates: compounds **1**−**3** and **5** melt at very low temperatures, between 100 and 150 °C; in contrast, thiolates bearing sterically demanding ligands melt at significantly higher temperatures (e.g., [Mg(STriph)$_2$]$_2$ melts above 300 °C).[24] This intricate connection of structure and function in the target molecules and the insight into how structural parameters can be influenced make it now possible to design more suitable reagents and precursor materials. The low melting points of the target compounds make them ideally suited precursors for the deposition of magnesium sulfides in a thermolysis regimen. The target molecules display close structural similarities to the well-studied organometallic magnesium derivatives, which also display a rich structural chemistry.

Supporting Information Available: Full tables of data collection parameters, atom coordinates, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters (65 pages). Ordering information is given on any current masthead page.

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