

Syntheses, Structures, and Reactivities of Heteroleptic Magnesium Amide Thiolates

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The syntheses and characterizations of a family of novel heteroleptic magnesium amide thiolates are presented. The compounds are synthesized by ligand redistribution chemistry involving reactions of equimolar amounts of magnesium amides and magnesium thiolates. Utilization of the smaller thiolates $[\text{Mg}(\text{SPh})_2]_n$ and $[\text{Mg}(\text{S}-2,4,6\text{-}^i\text{Pr}_3\text{C}_6\text{H}_2)_2]_n$ results in the isolation of dimeric species, $[\text{Mg}(\text{THF})(\text{N}(\text{SiMe}_3)_2)(\mu\text{-SR})_2]$ ($\text{R} = \text{Ph}$ (**1**), 2,4,6- $^i\text{Pr}_3\text{C}_6\text{H}_2$ (**2**)), with four-coordinate metal centers and bridging thiolate functions. The sterically more encumbered thiolate S-2,4,6- $^i\text{Bu}_3\text{C}_6\text{H}_2$ induces the formation of the four-coordinate, monomeric species $\text{Mg}(\text{THF})_2(\text{N}(\text{SiMe}_3)_2)(\text{S}-2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2)$ (**3**). Careful choice of reaction conditions allows the successful syntheses of pure heteroleptic compounds; however, it remains difficult to obtain the compounds in high yields, since a tendency toward product symmetrization and ligand redistribution under re-formation of the starting materials is prevalent. One of these symmetrized products is also included in this report: the dimeric, four-coordinate magnesium thiolate $[\text{Mg}(\text{THF})(\text{S}-2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2)(\mu\text{-S}-2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2)]_2$ (**4**), isolated as the product of the reaction between $[\text{Mg}(\text{N}(\text{SiMe}_3)_2)_2]$ and $\text{Mg}(\text{THF})_2(\text{S}-2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2)_2$. All compounds were characterized by NMR and IR spectroscopy, elemental analyses, and X-ray crystallography. Crystal data obtained with Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation are as follows. **1**: $\text{C}_{16}\text{H}_{31}\text{MgNOSSi}_2$, $a = 11.2100(1) \text{ \AA}$, $b = 17.4512(3) \text{ \AA}$, $c = 11.2999(2) \text{ \AA}$, $\beta = 97.952(1)^\circ$, $V = 2189.32(6) \text{ \AA}^3$, $Z = 4$, monoclinic, space group $P2_1/n$, R1 (all data) = 0.0934. **2**: $\text{C}_{25}\text{H}_{49}\text{MgNOSSi}_2$, $a = 11.1691(1) \text{ \AA}$, $b = 11.0578(1) \text{ \AA}$, $c = 26.0671(4) \text{ \AA}$, $\beta = 99.906(1)^\circ$, $V = 3171.44(6) \text{ \AA}^3$, $Z = 4$, monoclinic, space group $P2_1/c$, R1 (all data) = 0.0557. **3**: $\text{C}_{36}\text{H}_{71}\text{MgNO}_3\text{SSi}_2$, $a = 42.8293(16) \text{ \AA}$, $b = 10.9737(5) \text{ \AA}$, $c = 16.8305(7) \text{ \AA}$, $\beta = 98.755(3)^\circ$, $V = 7818.1(6) \text{ \AA}^3$, $Z = 8$, monoclinic, space group $C2/c$, R1 (all data) = 0.1331. **4**: $\text{C}_{80}\text{H}_{132}\text{Mg}_2\text{O}_2\text{S}_4$, $a = 18.8806(2) \text{ \AA}$, $b = 19.3850(2) \text{ \AA}$, $c = 27.3012(4) \text{ \AA}$, $\beta = 97.250(1)^\circ$, $V = 9912.4(2) \text{ \AA}^3$, $Z = 4$, monoclinic, space group $P2_1/n$, R1 (all data) = 0.1023.

Introduction

The first structural characterization of a magnesium thiolate was published about 10 years ago.¹ Since then, about a dozen of such reports have appeared in the literature, involving a wide variety of ligands and donors.^{2–10} The analysis of structural features displayed in these complexes (see Table 1 for a summary) indicates ligand bulk as the main structure-determining factor. Employment of very sterically encumbered ligands allows the isolation of compounds with very low coordination numbers, as observed in the pseudo-two-coordinate $\text{Mg}(\text{S}-2,6\text{-Triph}_2\text{C}_6\text{H}_3)_2$ (Triph = 2,4,6- $^i\text{Pr}_3\text{C}_6\text{H}_2$)⁵ or three-coordinate $[\text{Mg}(\text{STriph})(\mu\text{-STriph})_2]$ (Triph = 2,4,6- $\text{Ph}_3\text{C}_6\text{H}_2$).⁷ Both compounds display arene interactions between the ortho substituents

of the ligand and the metal center. Sterically demanding ligands are also needed to form compounds with a coordination number of 4, as evidenced by $\text{Mg}(\text{Et}_2\text{O})_2(\text{SMes}^*)_2$ ⁷ ($\text{Mes}^* = 2,4,6\text{-}^i\text{Bu}_3\text{C}_6\text{H}_2$), $\text{Mg}(\text{HMPA})_2(\text{SSiPh}_3)_2$,¹¹ (HMPA = hexamethylphosphoramide), and others (see Table 1). If smaller ligands are utilized, compounds with coordination numbers 5–7 are obtained.

Interest in the area of magnesium chalcogenolate chemistry was sparked by the discovery that the band gaps of ZnS and ZnSe semiconductors can be modulated by magnesium doping. The resulting quaternary phases $\text{Zn}_{2n-x}\text{Mg}_x\text{SSe}$ ($x = \text{trace amount}$) are important components in the production of blue-green lasers and diodes.^{12–15} However, use of the quaternary materials in these applications has been hampered by the presence of impurities and defects caused by nonideal starting materials. Current precursors for the preparation of quaternary materials by CVD techniques are magnesocene and diethylzinc, as the metal sources, in addition to hydrogen sulfide and elemental selenium.

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- (1) Knotter, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1990**, *112*, 5895.
- (2) Janssen, M. D.; Grove, D. M.; van Koten, G. In *Progress in Inorganic Chemistry*; Karlin, K., Eds.; Wiley and Sons: New York, 1997; Vol. 46, p 97.
- (3) Ruhlandt-Senge, K. *Comments Inorg. Chem.* **1997**, *19*, 351.
- (4) English, U.; Ruhlandt-Senge, K. *Coord. Chem. Rev.*, in press.
- (5) Niemeyer, M.; Power, P. P. *Inorg. Chim. Acta* **1997**, *263*, 201.
- (6) Ghosh, P.; Parkin, G. *Chem. Commun.* **1996**, 1239.
- (7) Ruhlandt-Senge, K. *Inorg. Chem.* **1995**, *34*, 3499.
- (8) Chadwick, S.; English, U.; Senge, M. O.; Noll, B. C.; Ruhlandt-Senge, K. *Organometallics* **1998**, *17*, 3077.
- (9) Chadwick, S.; English, U.; Ruhlandt-Senge, K. *Inorg. Chem.* **1999**, *38*, 6289.
- (10) Janssen, M. D.; van der Rijst, R.; Spek, A. L.; Grove, D. M.; van Koten, G. *Inorg. Chem.* **1996**, *35*, 3436.

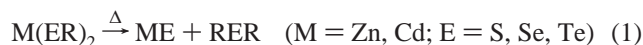
- (11) Chadwick, S.; Ruhlandt-Senge, K. Unpublished work.
- (12) Kozlovsky, V. I.; Krysa, A. B.; Korostelin, Y. V.; Shapkin, P. V.; Kalisch, H.; Luenenburger, M.; Heuken, M. *J. Cryst. Growth* **1998**, *184/185*, 124.
- (13) Soellner, J.; Schmoranzler, J.; Hamadeh, H.; Bollig, B.; Kubalek, E.; Heuken, M. *J. Electron. Mater.* **1995**, *24*, 1557.
- (14) (a) Kijima, S.; Kawasumi, T.; Asano, T.; Toda, A.; Funato, K. (Heisei). Jpn. Kokai Tokkyo JP 09092930A2 19970404, 1995. (b) Yoshie, M.; Hisida, Y. Jpn. Kokai Tokkyo Koho JP 94-55172 19940228, 1997.
- (15) Toda, A.; Asano, T.; Funato, K.; Nakamura, F.; Mori, Y. *J. Cryst. Growth* **1994**, *145*, 537.

Table 1. Selected Geometrical Details for Compounds 1–4 and Related Species

compound	aggr no.	CN	Mg–E (Å)	D	Mg–D (Å)	ref
Mg(S-2,6-Trip ₂ C ₆ H ₃) ₂	1	2+ar ^d	2.33	arene	2.69–2.79	5
[Mg(Tp ^{p-Tol})SH]	1	4	2.35	N(Tp ^{p-Tol})	2.10	6
Mg(Et ₂ O) ₂ (SMes*) ₂	1	4	2.39	Et ₂ O	2.07	7
Mg(HMPA) ₂ (SSiPh ₃) ₂	1	4	2.43	HMPA	1.94	11
Mg(THF) ₂ (N(SiMe ₃) ₂)(SMes*)	1	4	2.43	THF	2.05	<i>h</i>
[C ₇ H ₉ NH] ₂ [Mg(SC ₆ F ₅) ₄]	1	4	2.45			8
Mg(py) ₃ (SC ₆ F ₅) ₂	1	5	2.49	py	2.17	8
Mg(py) ₂ (S-2-NC ₅ H ₄) ₂	1	6	2.62	N ^a	2.17	8
				py	2.20	
Mg(py) ₄ (SPh) ₂	1	6	2.63	py	2.29	8
Mg(py) ₄ (SC ₆ F ₅) ₂	1	6	2.65	py	2.28	42
Mg(15C5)(SCPh ₃) ₂ ^c	1	7	2.66	15C5	2.18	9
[Mg(15C5)(THF) ₂][SMes*] ₂	1	7		15C5	2.17	9
				THF	2.09	
[Mg(STrip) ₂] ₂	2	3+ar	2.35 ^t	arene	2.56, 2.80	7
			2.46 ^{br}			
[(CuMes) ₄ (μ-SC ₆ H ₄ (CH(Me)NMe ₂)-2) ₂ (Mg(SC ₆ H ₄ (CH(Me)NMe ₂)-2)) ₂]	2	4	2.38 ^t	N ^a	2.18	1
			2.43 ^{br}			
[Mg(THF)(SMes*) ₂] ₂	2	4	2.37 ^t	THF	2.03	<i>b</i>
			2.50 ^{br}			
[Mg(THF)(N(SiMe ₃) ₂)(STrip)] ₂	2	4	2.51 ^{br}	THF	2.05	<i>b</i>
[Mg(THF)(N(SiMe ₃) ₂)(SPh)] ₂	2	4	2.53 ^{br}	THF	2.03	<i>b</i>
[Mg(SC ₆ H ₄ -2-CH ₂ NMe ₂) ₂] ₂	2	5	2.45 ^t	N ^a	2.25	10
			2.55 ^{br}			
[Mg ₃ (py) ₆ (η ² -SPh) ₆]	3	6	2.61 ^{br}	py	2.22	8

^a Superscript notation: a = intramolecular interaction, t = terminal, br = bridging. ^b This work. ^c 15C5 = 15-crown-5. ^d ar = arene.

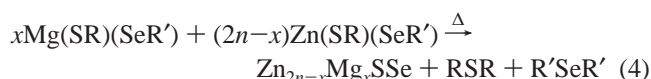
In view of the problems associated with the current starting materials, a search for convenient alternative routes able to provide pure quaternary materials with the desired degrees of magnesium doping is warranted. One synthetic approach to ZnS or ZnSe semiconductors involves the thermolysis of the appropriate chalcogenolates, as demonstrated with the deposition of various zinc and cadmium derivatives (eq 1).¹⁶ Consequently,



thermolysis of appropriate mixtures of zinc and magnesium chalcogenolates may be a suitable route for the preparation of pure quaternary materials. To explore the suitability of the thermolysis route for the production of tailored quaternary materials, development of synthetic routes to the currently unknown heteroleptic thiolate selenolates Zn(SR)(SeR') and Mg(SR)(SeR') appears to be indicated. Possible synthetic approaches to the thiolate selenolates involve a heteroleptic amide thiolate, convertible to the thiolate selenolate by simple transamination (eq 2) or ligand redistribution chemistry (eq 3).



Quaternary materials would then be producible by thermolysis of appropriate mixtures of zinc and magnesium thiolate selenolates (eq 4).



Few heteroleptic compounds are known, possibly because of their tendency to form symmetrized products by ligand redistribution. In this report, we present the syntheses and structural characterizations of the first magnesium amide thiolates, namely,

[Mg(THF)(N(SiMe₃)₂)(SPh)]₂ (**1**), [Mg(THF)(N(SiMe₃)₂)(S-2,4,6-*t*-Pr₃C₆H₂)]₂ (**2**), and Mg(THF)₂(N(SiMe₃)₂)(S-2,4,6-*t*-Bu₃C₆H₂) (**3**)—rare examples of heteroleptic magnesium derivatives. Synthetic approaches to the thiolate selenolates are also reported, as are the synthesis and structural characterization of the dimeric species [Mg(THF)(S-2,4,6-*t*-Bu₃C₆H₂)(μ-S-2,4,6-*t*-Bu₃C₆H₂)]₂ (**4**), the product of a ligand redistribution reaction.

Experimental Section

General Procedures. All reactions were performed under a purified nitrogen atmosphere by using modified Schlenk techniques and/or a Braun Labmaster 100 drybox. *n*-Hexane, toluene, and tetrahydrofuran (THF) were distilled just prior to use from a Na/K alloy, followed by two freeze–pump–thaw cycles. Commercially available HSPH was stored over molecular sieves (4 Å) and distilled prior to use. HSTrip, HSMes*, and HSeMes* were prepared according to literature procedures.^{17–21} The magnesium thiolates Mg(THF)₂(SPh)₂,²² [Mg(STrip)₂]_n,²² and [Mg(SMes*)₂]₂⁷ were prepared by combining commercially available (ⁿBu/ⁿBu)₂Mg (1 M solution of a mixture containing *n*-butyl and *sec*-butyl in heptane, Aldrich) with 2 equiv of the respective thiols. The phenyl derivative Mg(THF)₂(SPh)₂ was prepared in THF, since the donor-free, polymeric [Mg(SPh)₂]_n exhibits only marginal solubility in hydrocarbon solvents. The two other thiolates were prepared in hexanes. The purity of all compounds was confirmed by ¹H NMR spectroscopy. [Mg(N(SiMe₃)₂)₂]₂ was prepared by a slightly modified literature procedure.^{23,24} ¹H and ¹³C NMR spectra were recorded on a Bruker DPX-300 spectrometer, and infrared spectra were acquired for samples in Nujol mulls between KBr plates on a Perkin-Elmer PE 1600 FT-IR spectrometer. Satisfactory elementary analyses were obtained for compounds 1–4.

- (17) Baas, J. M. A.; van Bekkum, H.; Hofnagel, M. A.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1110.
- (18) Rundel, W. *Chem. Ber.* **1968**, *101*, 2956.
- (19) Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 3683.
- (20) DuMont, W. W.; Kubiniok, S.; Lange, L.; Pohl, S.; Saak, W.; Wagner, I. *Chem. Ber.* **1991**, *124*, 1315.
- (21) Blower, P. J.; Dilworth, J. R.; Hutchinson, J. P.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1533.
- (22) Teng, W.; Ruhlandt-Senge, K. Unpublished work.
- (23) Wannagat, U.; Autzen, H.; Wismar, H.-J. *Z. Anorg. Allg. Chem.* **1972**, *394*, 254.
- (24) Wannagat, U.; Kuckertz, H. *Angew. Chem.* **1963**, *75*, 95.

Preparations. (a) [Mg(THF)(N(SiMe₃)₂(SPh))₂ (1). A 0.5 mmol sample of [Mg(N(SiMe₃)₂)₂] (0.345 g) and 1 mmol of Mg(THF)₂(SPh)₂ (0.386 g) were combined in a flask, followed by the addition of 30 mL of hexane. The resulting turbid solution was stirred for 4 h, heated to reflux temperature, and filtered hot through a Celite-padded filter frit. The clear filtrate was then transferred to a -20 °C freezer. Within 1 week, colorless crystals formed in low yield (≈15%). In attempts to increase the product yield, reaction conditions and solvents were varied. In one instance, the reaction was carried out in a THF/hexane mixture, a reaction condition chosen to increase the solubility of Mg(SPh)₂(THF)₂. However, only symmetrized products, namely, Mg(THF)₂(N(SiMe₃)₂)₂ and Mg(THF)₂(SPh)₂, were identified in NMR spectroscopic studies. Characterization data for **1** follow. Mp: >370 °C dec. ¹H NMR (C₆D₆), δ (ppm): 7.84 (d, 2H, *o*-H), 7.00 (t, 2H, *m*-H), 6.86 (t, 1H, *p*-H), 3.53 (br m, 4H, THF), 0.94 (br m, 4H, THF), 0.49 (s, 18H, N(SiMe₃)₂). ¹³C NMR (C₆D₆), δ (ppm): 135.73, 134.15, 128.86, 125.09, 68.02, 24.66, 6.34. IR (KBr plates, Nujol mull), cm⁻¹: 2922 (s), 2853 (s), 1462 (s), 1377 (m), 1239 (w), 1022 (w), 995 (w), 886 (w), 873 (w), 830 (w), 740 (w), 722 (w), 664 (w).

(b) [Mg(THF)(N(SiMe₃)₂(STrip))₂ (2). A 0.25 mmol sample of [Mg(N(SiMe₃)₂)₂] (0.17 g) was dissolved in 20 mL of hexane, and a 0.25 mmol sample of [Mg(STrip)₂] (0.29 g) was dissolved in 20 mL of the same solvent in a second flask. The magnesium amide solution was then slowly combined with the thiolate solution, yielding a white suspension. After the addition of a few drops of THF, the cloudiness disappeared. The resulting almost clear, pale yellow solution was stirred overnight at room temperature, followed by filtration over a Celite-padded filter frit. The filtrate was then stored at -20 °C; 0.48 g of colorless crystals were obtained within a few hours (0.83 mmol, 83% yield). Mp: 109–113 °C. ¹H NMR (C₆D₆), δ (ppm): 7.20 (s, 2H, *m*-H), 4.48 (sep, 2H, *o*-CH, ⁱPr), 3.64 (br m, 8H, THF), 2.93 (sep, 1H, *p*-CH, ⁱPr), 1.55 (d, 12H, *o*-CH₃, ⁱPr), 1.37 (d, 6H, *p*-CH₃, ⁱPr), 1.24 (br m, 8H, THF), 0.35 (s, 18H, N(SiMe₃)₂). ¹³C NMR (C₆D₆), δ (ppm): 150.88, 120.78, 70.10, 35.07, 33.13, 25.38, 25.08, 24.46, 6.64. IR (KBr plates, Nujol mull), cm⁻¹: 2923 (s), 2855 (s), 1459 (s), 1421 (w), 1378 (m), 1356 (w), 1306 (w), 1238 (s), 1106 (m), 1058 (w), 1019 (m), 1000 (s), 917 (w), 889 (s), 870 (s), 827 (s), 782 (w), 759 (w), 748 (w), 665 (m).

(c) Mg(THF)₂(N(SiMe₃)₂(SMes*)) (3). A 0.25 mmol sample of [Mg(N(SiMe₃)₂)₂] (0.17 g) was dissolved in 20 mL of hexane. In a second flask, 0.25 mmol of [Mg(SMes*)₂] (0.29 g) was dissolved in 20 mL of hexane, yielding a cloudy solution, which upon addition of a few drops of THF became clear. The two solutions were combined, and the mixture was stirred overnight at room temperature, followed by filtration over a Celite-padded filter frit. The resulting pale yellow filtrate was then stored at -20 °C, yielding 0.34 g (0.56 mmol, 56.4% yield) of colorless crystals. Mp: 146–148 °C. ¹H NMR (C₆D₆), δ (ppm): 7.51 (s, 2H, *m*-H), 3.50 (br m, 8H, THF), 1.99 (s, 18H, *o*-CH₃, ⁱBu), 1.37 (s, 9H, *p*-CH₃, ⁱBu), 1.22 (br m, 8H, THF), 0.31 (s, 18H, N(SiMe₃)₂). ¹³C NMR (C₆D₆), δ (ppm): 152.63, 143.86, 139.89, 121.79, 70.02, 38.97, 35.07, 32.77, 32.27, 25.43, 6.54. IR (KBr plates, Nujol mull), cm⁻¹: 29.24.4 (s), 2854 (s), 1461 (s), 1378 (m), 1350 (w), 1239 (w), 1182 (w), 1040 (w), 1017 (m), 991 (w), 920 (w), 873 (m), 841 (w), 754 (w), 420 (w).

(d) [Mg(THF)(SMes*)(μ-SMes*))₂ (4). Initially, compound **4** was isolated as the product of a reaction between equimolar amounts of [Mg(N(SiMe₃)₂)₂] and Mg(THF)₂(SMes*)₂. Upon identification, **4** was synthesized in a rational manner: A 0.28 g sample of HSMes* (1 mmol) was dissolved in 20 mL of hexane. A 0.5 mL (0.5 mmol, 1 M solution in heptane) portion of (ⁱBu/ⁱBu)₂Mg was added, whereupon a slightly turbid solution formed. Then 1 mmol of THF was added (1 mL of a stock solution prepared by mixing 1.6 mL of THF in 20 mL of hexane), and the solution cleared. The reaction mixture was refluxed for 3–4 h, after which the solvent was removed under vacuum, yielding a white solid. The solid was recrystallized from hexane, resulting in 0.23 g (0.389 mmol, 78%) of colorless crystals. Mp: 184–186 °C. ¹H NMR (C₆D₆), δ (ppm): 7.47 (s, 2H, *m*-H), 3.34 (br m, 4H, THF), 1.92 (s, 18H, *o*-C(CH₃)₃), 1.75 (br m, 4H, THF), 1.39 (s, 9H, *p*-C(CH₃)₃). ¹³C NMR (C₆D₆), δ (ppm): 152.90, 143.92, 139.92, 121.70, 70.20, 38.98,

35.09, 32.50, 32.33, 25.40. IR (KBr plates, Nujol mull), cm⁻¹: 2922 (s), 2852 (s), 1590 (w), 1538 (w), 1462 (m), 1376 (w), 1043 (w), 722 (w).

X-ray Crystallographic Studies. X-ray-quality crystals for all compounds were grown as described in the Experimental Section. The crystals of each compound were removed from the Schlenk tube under a stream of N₂ and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and immediately placed in the low-temperature N₂ stream of the diffractometer.²⁶ The intensity data sets for all compounds were collected using a Siemens SMART system, complete with a three-circle goniometer and a CCD detector operating at -54 °C. The data sets for compounds **1** and **2** were collected at -123 °C, utilizing a Cryojet low-temperature device from Oxford Instruments. Data for compounds **3** and **4** were collected at -182 and -183 °C, respectively, using a custom-built low-temperature device from Professor H. Hope (UC Davis). In all cases, graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) was employed. The data collections nominally covered a hemisphere of reciprocal space utilizing a combination of three sets of exposures, each with a different φ angle and each covering 0.3° in ω. Crystal decay was monitored by repeating the initial frames at the end of each data collection and analyzing the duplicate reflections. In all cases, no decay was observed. Absorption corrections were applied for **2** and **4** with the program SADABS.²⁷ The crystal structures of all compounds were solved by Direct Methods, as included in the SHELXTL-Plus program package.²⁸ Missing atoms were located in subsequent difference Fourier maps and included in the refinements. The structures of all compounds were refined by full-matrix least-squares calculations on F² (SHELX-93).²⁹ Hydrogen atoms were placed geometrically and refined using a riding model, including free rotation about C–C bonds for methyl groups with U_{iso} values constrained to 1.2 times the U_{eq} values of the carrier C atoms for nonmethyl groups and to 1.5 times the U_{eq} values of the carrier C atoms for methyl groups. The crystallographic programs used for structure refinements and solutions were installed on a Silicon Graphics Indigo² R10000 Solid Impact or a PC clone. Scattering factors were those provided with the SHELX program system. All non-hydrogen atoms, with the exception of some in disordered or restrained positions, were refined anisotropically. Disorder was typically handled by including split positions for the affected groups and included in the refinement of the respective occupancies. Generally, a set of restraints was applied to aid in modeling the disorder. Compound **3** contains a THF solvent molecule, which was described with all positions occupied by carbon atoms, since it was impossible to assign one as oxygen. Compounds **1** and **3** were identified as nonmerohedral twins. The two twin components can be interconverted by a rotation of 180° about the reciprocal *c* axis. The orientation matrices of the twin components were determined using a set of 999 reflections, of which about half fit the first component. To determine the second orientation matrix, the reflections of the first component were eliminated and the remaining second half of the reflections were indexed to the same cell, but in a different orientation. Further data evaluation and processing were performed with programs developed by Sparks³⁰ (TWIND, TWROT, TWUTIL, TWHKL). The refined matrices were used in SAINT to identify reflections belonging to the two twin components. The resulting two *hkl* files were combined into a new data set by using TWHKL, flagging reflections according to the twin component, and rejecting all partially overlapped reflections. Initially, the structures were solved using data belonging to the stronger diffracting twin component by Direct Methods (SHELXS-97) and refined with all non-hydrogen atoms

(25) Engelhard, L. M.; Jolly, B. S.; Junk, P. C.; Raston, C. L.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1986**, *39*, 1337.

(26) Hope, H. *Prog. Inorg. Chem.* **1994**, *41*, 1.

(27) Sheldrick, G. M. *SADABS: Program for Absorption Correction Using Area Detector Data*; University of Göttingen: Göttingen, Germany, 1996.

(28) *SHELXTL-Plus: Program Package for Structure Solution and Refinement*; Siemens: Madison, WI, 1996.

(29) Sheldrick, G. M. *SHELXL-93: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993.

(30) Sparks, R. A. *Sparks' Twinning Programs*; Bruker, AXS, Inc.: Madison, WI, 1996.

Table 2. Crystallographic Data for Compounds **1–4**^a

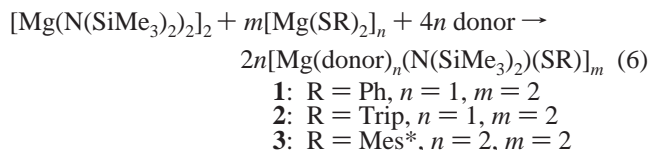
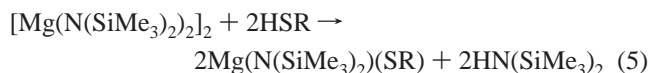
	1	2	3	4
formula	C ₁₆ H ₃₁ MgNOSSi ₂	C ₂₅ H ₄₉ MgNOSSi ₂	C ₃₆ H ₇₁ MgNO ₃ SSi ₂	C ₈₀ H ₁₃₂ Mg ₂ O ₂ S ₄
fw	365.97	492.20	678.49	1302.72
space group (No.)	<i>P</i> 2 ₁ / <i>n</i> (14)	<i>P</i> 2 ₁ / <i>c</i> (14)	<i>C</i> 2/ <i>c</i> (15)	<i>P</i> 2 ₁ / <i>n</i> (14)
<i>a</i> (Å)	11.2100(1)	11.1691(1)	42.8293(16)	18.8806(2)
<i>b</i> (Å)	17.4512(3)	11.0578(1)	10.9737(5)	19.3850(2)
<i>c</i> (Å)	11.2999(2)	26.0671(4)	16.8305(7)	27.3012(4)
β (deg)	97.952(1)	99.906(1)	98.755(3)	97.250(1)
<i>V</i> (Å ³)	2189.32(6)	3171.44(6)	7818.1(6)	9912.4(2)
<i>Z</i>	4	4	8	4
<i>d</i> _{calc} (g/cm ³)	1.110	1.031	1.153	1.089
lin abs coeff (mm ⁻¹)	0.287	0.213	0.194	0.154
<i>T</i> (K)	150	150	91	90
R1, wR2 (all data)	0.0934, 0.2667	0.0557, 0.1039	0.1331, 0.2257	0.1023, 0.2043
R1, wR2 (>2 σ)	0.0844, 0.2484	0.0398, 0.0982	0.0742, 0.1865	0.0764, 0.1903

^a Radiation: Mo K α ($\lambda = 0.71073$ Å). R1 = $\sum||F_o| - |F_c||/\sum|F_o|$; wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)]^{1/2}$.

taken as anisotropic, resulting in wR2 = 0.45 for compound **3**. Besides many other oddities, the difference Fourier map showed a peak of about 2 e far removed from any “heavy” atom close to any fragment of the main molecule. Using the data set that combined the data of both twin components solved the problem, and the twinning ratio was refined to 0.6:0.4. The difference map cleared up, the standard uncertainties for the bond lengths and angles dropped by about 50%, and wR2 decreased from 0.45 to 0.22 for all data. The technique described in detail for compound **3** was applied analogously to the case of **1** with similar results. Absorption corrections for the twinned structures were not applied. Further details of the refinements and how disorder and twinning were handled are outlined in the Supporting Information. Selected details of the data collections and refinements are given in Table 2, and selected geometrical parameters are provided in Table 1.

Results

Synthetic Aspects and Reactivities. Possible synthetic routes to the target compounds involve either thiolysis (eq 5) or ligand redistribution (eq 6). Initial attempts to prepare the target



compounds focused on the thiolysis route (eq 5). This scheme did not prove successful in our hands, yielding only product mixtures. The outcome did not change even after careful attempts to control the reaction conditions either by slow, dilute addition of the thiol to the metal amide or by lowering the reaction temperature to -78 °C, or by both. Consequently, the synthetic approach was changed, and ligand redistribution chemistry involving reactions of equimolar amounts of the magnesium amide $[\text{Mg}(\text{N}(\text{SiMe}_3)_2)_2]_2$ and the appropriate magnesium thiolates were employed for the syntheses of compounds **1–3**. However, the preparation of these compounds still proved problematic. For example, the reactions of $[\text{Mg}(\text{N}(\text{SiMe}_3)_2)_2]_2$ with equimolar amounts of $[\text{Mg}(\text{SPh})_2]_n$ in hexane/THF solvent mixtures yielded only symmetrized products, as indicated by crystallographic and NMR analyses (eq 7). NMR studies indicated that heteroleptic **1** was formed initially, but only the symmetrized thiolate and amide could be isolated. Compound **1** was obtained in pure form, but in low yields if $[\text{Mg}(\text{N}(\text{SiMe}_3)_2)_2]_2$ was reacted with $\text{Mg}(\text{THF})_2(\text{SPh})_2$ in pure hexane. In contrast, the reaction of $[\text{Mg}(\text{N}(\text{SiMe}_3)_2)_2]_2$

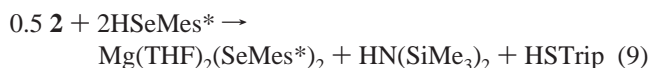
with $\text{Mg}(\text{THF})_2(\text{SMes}^*)_2$ in a toluene/hexane mixture yielded the symmetrized dimer **4**, while the reaction of $[\text{Mg}(\text{N}(\text{SiMe}_3)_2)_2]_2$ with $[\text{Mg}(\text{SMes}^*)_2]_2$ in a hexane/THF mixture led to the almost quantitative isolation of pure **3**.



In an attempt to utilize the amido functionality in **1–3** for the syntheses of the heteroleptic magnesium thiolate selenolates $\text{Mg}(\text{SR})(\text{SeR})$, **2** was treated with an equimolar amount of freshly reduced HSeMes* (eq 8). NMR analysis of the solid



reaction product showed however only resonances for the selenolate ligand and THF donor. Both, the Mes* and THF signals agreed perfectly with the previously reported spectrum of $\text{Mg}(\text{THF})_2(\text{SeMes}^*)_2$, which was synthesized by reacting either (^{*t*}Bu/^{*n*}Bu)₂Mg or $[\text{Mg}(\text{N}(\text{SiMe}_3)_2)_2]_2$ with 2 or 4 equiv of HSeMes*, respectively.⁷ The isolation of the pure selenolate indicates that the selenol replaces not just the amide but also the thiolate (eq 9).



A second attempt to achieve the syntheses of the heteroleptic thiolate selenolates under very carefully controlled reaction conditions (slow, dilute additions of the selenols; reaction temperatures of -78 °C) gave identical results. Ligand redistribution reactions (eq 3) involving 1 equiv each of $\text{Mg}(\text{SR})_2$ and $\text{Mg}(\text{SeR})_2$ as an alternative route did not lead to the isolation of the target compounds; only symmetrized products were obtained.

Structural Aspects. Crystallographic information and data collection parameters for compounds **1–4** are summarized in Table 2 and the Experimental Section. A compilation of selected geometrical parameters for all compounds is given in Table 1, while Figures 1–4 illustrate the structural principles of compounds **1–4**, respectively.

(a) $[\text{Mg}(\text{THF})(\text{N}(\text{SiMe}_3)_2)(\text{SPh})]_2$ (**1**). Compound **1** crystallizes as a dimer with bridging thiolate units, as shown in Figure 1. A center of symmetry generates a planar four-membered ring, comprising of two magnesium and two sulfur atoms, with bridging magnesium–sulfur distances of 2.522(2) and 2.533(2) Å. The magnesium centers are four-coordinate and display terminal magnesium–nitrogen (amide) contacts of 2.001(3) Å

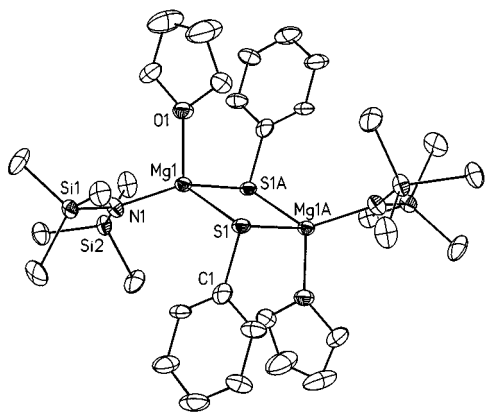


Figure 1. Computer-generated plot of **1** with anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity.

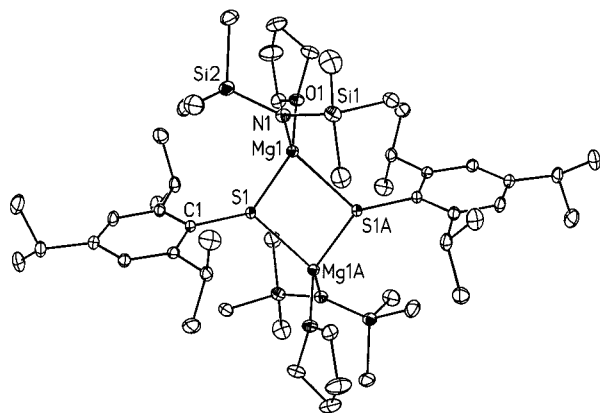


Figure 2. Computer-generated plot of **2** with anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity.

and magnesium–oxygen (THF) interactions of 2.028(3) Å. Angles within the four-membered ring are close to 90° (S–Mg–S 90.71(5), Mg–S–Mg 89.29(5)°).

(b) $[\text{Mg}(\text{THF})(\text{N}(\text{SiMe}_3)_2)(\text{STrip})]_2$ (**2**). Compound **2** was found to have a dimeric structure, as shown in Figure 2. Like compound **1**, this dimer contains a planar Mg_2S_2 ring, generated by a center of symmetry located in the center of the ring. The bridging magnesium–sulfur distances are 2.4978(5) and 2.5321(5) Å, while magnesium–nitrogen and –oxygen contacts are found to be 2.001(1) and 2.050(1) Å, respectively. The angles within the four-membered Mg_2S_2 ring are acute for S–Mg–S (79.58(2)°) and obtuse for Mg–S–Mg (100.42(2)°) and obtuse for Mg–S–Mg (100.42(2)°).

(c) $\text{Mg}(\text{THF})_2(\text{N}(\text{SiMe}_3)_2)(\text{SMes}^*)$ (**3**). Compound **3** crystallizes as a monomeric unit, as shown in Figure 3. The magnesium center is surrounded in a distorted tetrahedral manner by one SMes^* ligand, with an Mg–S distance of 2.431(2) Å, an $\text{N}(\text{SiMe}_3)_2$ ligand, with an Mg–N contact of 1.998(3) Å, and two THF donors, displaying Mg–O bond lengths of 2.042(3) and 2.051(3) Å. The distortion in the magnesium environment involving the sterically demanding amide and thiolate ligands results in widened tetrahedral angles, while the angles involving the smaller THF donors are smaller than the typical tetrahedral value.

(d) $[\text{Mg}(\text{THF})(\text{S}-2,4,6\text{-Bu}_3\text{C}_6\text{H}_2)(\mu\text{-S}-2,4,6\text{-Bu}_3\text{C}_6\text{H}_2)]_2$ (**4**). Compound **4**, shown in Figure 4, exhibits a dimeric structure with four-coordinate magnesium centers. Each magnesium is connected to three SMes^* ligands, one terminal and the other two bridging, thus forming a planar, four-membered ring of

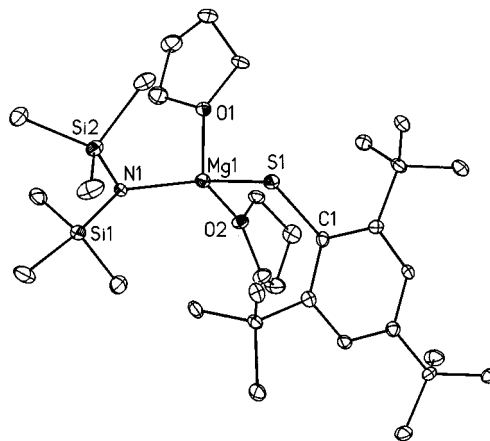


Figure 3. Computer-generated plot of **3** with anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity.

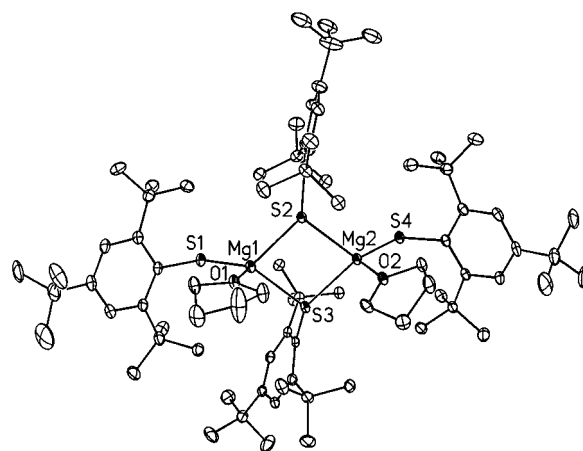


Figure 4. Computer-generated plot of **4** with anisotropic displacement parameters depicting 30% probability. Hydrogen atoms have been omitted for clarity.

alternating magnesium and sulfur centers. The coordination sphere at magnesium is completed by an additional THF molecule. The magnesium–sulfur bond lengths for the bridging contacts are significantly longer (2.51 Å average) than those for the terminal contacts (2.37 Å average). The magnesium–oxygen (THF) bond lengths are about 2.03 Å (average). The angles within the four-membered Mg_2S_2 ring are acute for S–Mg–S (82.43(4), 81.70(4)°) and obtuse for Mg–S–Mg (97.21(4), 98.33(4)°).

Discussion

Attempts to synthesize heteroleptic magnesium amide thiolates by thiolysis (eq 5) resulted in intractable product mixtures, while ligand redistribution chemistry (eq 6) led to the syntheses of compounds **1–3**. Even though **1–3** were isolated in good purity, the problems encountered during various synthetic attempts lead us to conclude that pure heteroleptic compounds are generally difficult to prepare, a viewpoint supported by the small number of well characterized derivatives in the literature. For example, Grützmacher et al. attempted to synthesize heteroleptic zinc amide thiolates using thiolysis chemistry³¹ but reported the formation of mixtures containing heteroleptic target compounds and unreacted starting materials, implying that in

(31) Grützmacher, H.; Steiner, M.; Pritzkow, H.; Zsolnai, L.; Huttner, G.; Sebald, A. *Chem. Ber.* **1992**, *125*, 2199.

none of the products did the amide:thiolate ratio resemble that of the starting materials. Problems were also encountered by Lappert et al. when reacting $[\text{Yb}(\text{N}(\text{SiMe}_3)_2)(\mu\text{-N}(\text{SiMe}_3)_2)_2]$ with 2 equiv of HO-BHT (BHT = 2,6-*t*-Bu₂-4-MeC₆H₂). The symmetrized product $[\text{Yb}(\text{O-BHT})(\mu\text{-O-BHT})_2]$ was isolated as the only product. In contrast, utilization of HOC'Bu₃ resulted in the isolation of the heteroleptic dimer.³²

A common structural feature in compounds **1–4** is the coordination number 4 for the metal center. As previously shown, this four-coordination environment for magnesium is only prevalent if sterically encumbered ligands are present, as demonstrated by $\text{Mg}(\text{THF})_2(\text{SMe}_3)_2$,⁷ $\text{Mg}(\text{Tp}^{p\text{-Tol}})\text{SH}$ ($\text{Tp}^{p\text{-Tol}}$ = tris(3-*p*-tolylpyrazolyl)hydroborate),⁶ $\text{Mg}(\text{HMPA})_2(\text{SSiPh}_3)_2$,¹¹ and a few other compounds (Table 1). The coordination number 4 in **1–3** can be rationalized by the presence of the sterically encumbered amido ligand $\text{N}(\text{SiMe}_3)_2$, whose size makes possible the isolation of the three-coordinate magnesium, calcium, strontium, and barium amides $[\text{Ae}(\text{N}(\text{SiMe}_3)_2)(\mu\text{-N}(\text{SiMe}_3)_2)_2]$ (Ae = Mg, Ca, Sr, Ba).^{33–36} The magnesium–sulfur distance in the monomeric complex **3** (2.431(2) Å) and the terminal Mg–S bond length in **4** (2.369(1) Å (average)) agree well with previously reported data for four-coordinate magnesium thiolates (Table 1). A similar agreement was found between the bridging Mg–S distances in **1**, **2**, and **4** and those in known magnesium thiolates (Table 1). Magnesium–nitrogen distances in the four-coordinate amide $\text{Mg}(\text{THF})_2(\text{N}(\text{SiMe}_3)_2)_2$ were reported to be 2.015(5) and 2.027(5) Å,³⁷ values only slightly larger than those for the corresponding distances in **1** (2.001(3) Å), **2** (2.001(1) Å), and **3** (1.998(3) Å). The slight bond shortening in **1–3** compared to $\text{Mg}(\text{THF})_2(\text{N}(\text{SiMe}_3)_2)_2$ might be explained on the basis of the reduced steric presence of the thiolate ligands (due to the longer Mg–S distances) as compared to the sterically very demanding $\text{N}(\text{SiMe}_3)_2$ ligand.

Interestingly, the bridging function in compounds **1** and **2** is performed by the thiolate ligands, the amide groups being in terminal positions. This commonly observed structural motif

in heteroleptic amide chalcogenolate chemistry was also reported for $[\text{Fe}(\text{N}(\text{SiMe}_3)_2)(\mu\text{-O-2,4,6-}^i\text{Bu}_3\text{C}_6\text{H}_2)_2]$,³⁸ $[\text{Pb}(\text{N}(\text{SiMe}_3)_2)(\mu\text{-OSiMe}_3)_2]$,³⁹ $[\text{M}_3(\text{N}(\text{SiMe}_3)_2)_2(\mu\text{-STrip})_4]$ (M = Zn, Fe),⁴⁰ $[\text{Zn}(\text{N}(\text{SiMe}_3)_2)(\mu\text{-ODipp})_2]$ (Dipp = 2,6-*i*-Pr₂C₆H₃),⁴¹ $[\text{Yb}(\text{N}(\text{SiMe}_3)_2)(\mu\text{-OC}^i\text{Bu}_3)_2]$, and $[\text{Gd}(\text{N}(\text{SiMe}_3)_2)_2(\mu\text{-S}^i\text{Bu})_2]$,⁴² along with others.

Conclusion

Three new heteroleptic magnesium amide thiolates were synthesized and characterized. The compounds displayed dimeric structures if sterically less demanding ligands were utilized but monomeric ones if ligands with increased steric demand were employed. The target compounds were most favorably synthesized by ligand redistribution chemistry, but even after successful isolation of the three heteroleptic target compounds, it remained difficult to control the product composition, since complex solution equilibria prompted the formation of not only the heteroleptic materials but also symmetrized products. Interestingly, the reaction conditions needed to isolate the heteroleptic target compounds varied with the ligand systems.

The initial motivation for this study was a desire to utilize the target compounds in the synthesis of heteroleptic magnesium thiolate selenolates, which would provide critical building blocks for the production of the important quaternary phases $\text{Zn}_{2n-x}\text{-Mg}_x\text{SSe}$ by thermolysis. However, problems encountered in isolating the heteroleptic target compounds in good yields illuminated difficulties connected with this route.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structures of complexes **1–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (32) van den Hende, J. R.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1994**, 1413.
 (33) Westerhausen, M.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1992**, 609, 39.
 (34) Westerhausen, M.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1991**, 606, 177.
 (35) Westerhausen, M.; Schwarz, W. *Z. Anorg. Allg. Chem.* **1991**, 604, 127.
 (36) Vaartstra, B. A.; Huffman, J. C.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, 30, 121.
 (37) Bradley, D. C.; Hursthouse, M. B.; Ibrahim, A. A.; Malik, K. M. A.; Motevalli, M.; Mösele, R.; Powell, H.; Runnacles, J. D.; Sullivan, A. C. *Polyhedron* **1990**, 9, 2959.

- (38) Bartlett, R. A.; Ellison, J. E.; Power, P. P.; Shoner, S. C. *Inorg. Chem.* **1991**, 30, 2888.
 (39) Weinert, C. S.; Guzei, I. A.; Rheingold, A. L.; Sita, L. R. *Organometallics* **1998**, 17, 498.
 (40) MacDonnell, F. M.; Ruhlandt-Senge, K.; Ellison, J. J.; Holm, R. H.; Power, P. P. *Inorg. Chem.* **1995**, 34, 1815.
 (41) Olmstead, M. M.; Power, P. P.; Shoner, S. C. *J. Am. Chem. Soc.* **1991**, 113, 3379.
 (42) Aspinall, H. C.; Bradley, D. C.; Hursthouse, M. B.; Sales, K. D.; Walker, N. P. C. *J. Chem. Soc., Chem. Commun.* **1985**, 1585.