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Formation of Separated versus Contact Ion Triplets in Magnesium Thiolates. Synthesis and Characterization of $[Mg(15\text{-crown-}5)(SCPh_3)_2]$ and $[Mg(15\text{-crown-}5)(THF)_2][S\text{-}2,4,6\text{-}tBu_3C_6H_2)]_2$

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The synthesis and structural characterization of two magnesium thiolate complexes are described. Both compounds were prepared by analogous reactions routes, namely, alkane elimination and transamination, but using differently sized ligands. Utilization of the smaller $HSCPh_3$, resulted in the formation of $[Mg(15\text{-crown-}5)(SCPh_3)_2]$, **1**, displaying a seven-coordinate magnesium center with two magnesium−sulfur bonds. Employment of the sterically more encumbered $HS\text{-}2,4,6\text{-}tBu_3C_6H_2$ yielded a separated cation and anions as displayed in $[Mg(15\text{-crown-}5)(THF)_2][S\text{-}2,4,6\text{-}tBu_3C_6H_2]_2$, **2**. Compound **2** exhibits a seven-coordinate cation, completing its coordination environment with five metal−crown-ether interactions in addition to two tetrahydrofuran (THF) contacts. The compounds were characterized by IR and NMR spectroscopy in addition to X-ray crystallography. Crystal data with Mo Kα ($\lambda = 0.710\,73$ Å) are as follows: **1**, $C_{48}H_{50}MgO_5S_2$, $a = 8.4785(4)$ Å, $b = 9.3595(5)$ Å, $c = 13.8306(6)$ Å, $\alpha = 87.332(1)°$, $\beta = 85.929(1)°$, $\gamma = 68.733(1)°$, $Z = 1$, triclinic; **2**, $C_{54}H_{94}MgO_7S_2$, $a = 13.6755(2)$ Å, $b = 12.8045(6)$ Å, $c = 32.7127(12)$ Å, $\beta = 97.87(1)°$, $Z = 4$, monoclinic.

Introduction

The molecular chemistry of alkaline earth derivatives has long been dominated by oxygen derivatives, fueled by the request for improved precursors for the high-temperature superconductor industry.[1,2] In contrast, chemistry concerned with the heavier chalcogen analogues has not received much attention,[1d,3,4] which is surprising considering their importance in the semiconductor,[5] phosphor,[6] or two-color-IR windows technology.[7] Specifically, magnesium thiolates and selenolates have been linked to improved precursors for blue-green lasers, since the band gap of conventional IIB−VIA materials can be modulated by alkaline earth metal inclusion, as demonstrated with the incorporation of magnesium into ZnS/ZnSe phases. The quaternary material may be obtained by the thermolysis of mixtures of zinc and magnesium thiolates and selenolates.[8] Importantly, the Zn:Mg ratio dictates the electronic properties of the final material, allowing the production of materials with finely tuned band gaps.[5]

Over the past decade about a dozen magnesium thiolates have been reported, including $[(CuMes)_4(\mu\text{-}SAr)_2(MgSAr)_2]$ (Mes $= 2,4,6\text{-}Me_3C_6H_2$, Ar $= SC_6H_4((R)CH(Me)NMe_2)$),[9] $[Mg(STriph)_2]_2$ (Triph $= 2,4,6\text{-}Ph_3C_6H_2$),[10] $Mg(SMes^*)_2(Et_2O)_2$ (Mes* $= 2,4,6\text{-}tBu_3C_6H_2$),[10] $[Mg(Tp^{p-Tol})SH]$ (Tp^{p-Tol} = tris(3-*p*-tolylpyrazolyl)hydroborate),[11] $[Mg\{S\text{-}2CH_2NMe_2C_6H_4\}_2]_2$,[12] $[(C_7H_9\text{-}NH)]_2[Mg(SC_6F_5)_4]$,[13] $Mg(SC_6F_5)_2(py)_3$ (py = pyridine),[13] $Mg(S\text{-}2\text{-}NC_5H_4)_2(py)_2$,[13] and $Mg_3(\eta^2SPh)_6(py)_6$.[13] The common

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theme in all compounds is a bond between the magnesium center and the thiolate ligands. Compounds with isolated alkaline earth cations and thiolate anions have, to the best of our knowledge, not been described.

In this paper, we report on the influence of ligand size on association properties in the solid state, resulting in the formation of either contact or separated alkaline earth thiolates. The detailed investigation of their structure−function relationship, specifically, how the ionic association can be influenced and predetermined, is critical for the development of well-suited precursors and the selected removal of specific alkaline earth ions from waste mixtures.

The formation of compounds displaying either metal−ligand interactions or a coordination sphere completed solely by donors was induced by using ligands with different degrees of steric bulk: the smaller ligand $HSCPh_3$ in conjunction with 15-crown-5 yielded a compound with magnesium−sulfur bonds, $[Mg(15\text{-crown-}5)(SCPh_3)_2]$, **1**, while the sterically more encumbered HSMes* with an identical set of donors induced separation of cation and anions as observed in $[Mg(15\text{-crown-}5)(THF)_2][SMes^*]_2$, **2**.

Experimental Section

General Procedures. All reactions were performed under a purified nitrogen atmosphere by using modified Schlenk techniques and a Braun Labmaster 100 drybox. Toluene, *n*-hexane, and tetrahydrofuran (THF) were distilled prior to use from a Na/K alloy followed by two freeze−pump−thaw cycles. Commercially available 15-crown-5 was dried over 3 Å molecular sieves. HSMes* was prepared according to literature procedures.[14] Commercially available $HSCPh_3$ was dried by warming under vacuum for several hours. Commercially available $(n\text{-Bu}/s\text{-Bu})_2Mg$ was used as a 1.0 M solution in heptane. $[Mg\{N(SiMe_3)_2\}_2]_2$ was prepared according to literature procedures.[15] ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded on a Bruker DPX-300 spectrometer. Infrared spectra were recorded as Nujol mulls between KBr plates on a Perkin-Elmer PE 1600 FT-IR spectrometer. Elemental analysis was precluded by the high moisture sensitivity of the compounds. For example, the 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.

$[Mg(15\text{-crown-}5)(SCPh_3)_2]$, 1. To a 100 mL Schlenk flask was added 0.35 g (0.5 mmol) of $[Mg\{N(SiMe_3)_2\}_2]_2$, 0.55 g (2.0 mmol) of $HSCPh_3$, and 0.25 g of 15-crown-5 (1 mmol). Approximately 20 mL of toluene and 10 mL of THF were added and stirred at room temperature for 2 h. Over the duration of the reaction, the solution developed a hazy turbidity and a deep yellow coloring. The reaction was filtered hot through a Celite padded frit and cooled to room temperature. Pale-yellow crystals quickly formed in 24% yield (0.19 g). Mp: the pale-yellow powder decomposed above 155 °C. An analogous result is achieved if $(n\text{-Bu}/s\text{-Bu})_2Mg$ is treated with 2 equiv of $HSCPh_3$ in the presence of 15-crown-5 and THF. ^1H NMR (py-d_5): δ 7.77−7.19 (broad overlapping resonances), 3.67 (s, 15-crown-5), correct integration. $^{13}C\{^1H\}$ NMR (py-d_5): δ 147.29, 131.46, 127.93, 126.80, 71.43. IR (cm^{-1}) (Nujol): 2904 s, 1593 m, 1462 s, 1377 s, 1349 w, 1260 w, 1180 w, 1089 s, 1038 m, 967 s, 840 w, 766 w, 735 m, 700 s, 671 w, 628 w, 529 w, 505 w.

$[Mg(15\text{-crown-}5)(THF)_2][SMes^*]_2$, 2. To a 100 mL Schlenk flask was added 0.56 g (2.0 mmol) of HSMes* and 0.22 g (1.0 mmol) of 15-crown-5. Approximately 10 mL of hexane and 15 mL of THF were added and stirred. $(n\text{-Bu}/s\text{-Bu})_2Mg$, 1.0 mL (1.0 mmol), was added dropwise, resulting in a cloudy, light yellow solution. The reaction was heated briefly to reflux and filtered immediately through a Celite padded frit. The homogeneous pale yellow filtrate yielded colorless plate-shaped crystals after sitting overnight at 0 °C in 28% yield (0.26 g). Mp: irreversible melt to a yellow oil at 160−165 °C. An analogous result is achieved if $[Mg\{N(SiMe_3)_2\}_2]_2$ is treated with 4 equiv of HSMes* in the presence of 15-crown-5 and THF. It is significant to note that the crystals lose THF upon removal of solvent, as noted in several attempts to prepare the sample with a correct stoichiometric amount of THF. In all cases, integration indicated a loss of about one THF donor, as compared to the crystallographic data. ^1H NMR (C_6D_6): δ 7.51 (4 H, s, m−H), 3.50−3.59 (4 H, m, THF), 3.17 (20 H, s, 15-crown-5), 2.02 (36 H, s, o-tBu), 1.34−1.43 (22 H, m, *p*-tBu, THF). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 32.26 (tBu), 32.50 (tBu), 39.27 ($C(CH_3)_3$), 66.74 (15-crown-5), 72.00 (THF), 121.00 (*m*-Ph), 135.95 (*p*-Ph), 151.35 (*o*-Ph). IR (cm^{-1}): 2934 s, 2856 s, 1586 w, 1462 s, 1379 m, 1357 w, 1243 w, 1186 w, 1085 s, 1044 m, 1018 m, 966 s, 921 w, 876 m, 756 w, 616 w.

X-ray Crystallographic Studies. X-ray quality crystals for all compounds were grown as described earlier in the Experimental 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).[16] A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and immediately placed in the low-temperature N_2 stream of the diffractometer. Data sets for both compounds were collected using a Siemens SMART system, complete with three-circle goniometer and CCD detector operating at −54 °C. The data sets were collected at 150 K using a Cryojet low-temperature device from Oxford Instruments by employing graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). 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 exposure covering 0.3° in ω. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analyzing the duplicate reflections. In all cases, no decay was observed. An absorption correction was applied utilizing the program SADABS.[17] The crystal structures of all compounds were solved by direct methods, as included in the SHELX program package.[18,19] Missing atoms were located in subsequent difference Fourier maps and included in the refinement. The structures were refined by full-matrix least-squares refinement on F^2 (SHELX 93).[18,19] Hydrogen atoms were placed geometrically and refined using a riding model, including free rotation of methyl groups. The hydrogen atoms in all compounds 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. Scattering factors were those provided by the SHELX program.[18,19] All non-hydrogen atoms were refined anisotropically. Disorder was observed in the crown ether part of **1**, where a center of symmetry located at magnesium resulted in two crown ether positions. The disorder was handled by including split positions. A set of restraints was applied to aid in the modeling of the crown. Further details about the refinements and how disorder was handled are outlined in the Supporting Information. Crystallographic parameters for compounds **1** and **2** are summarized in Table 1, while selected bond distances and angles can be found in Table 2.

Results

Compounds **1** and **2** can be prepared using two different synthetic approaches: (1) alkane elimination involving the reaction of dibutylmagnesium $(n\text{-Bu}/s\text{-Bu})_2Mg$ with 2 equiv of

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Table 1. Crystallographic Data for Compounds **1** and **2**[a]

	1	**2**
formula	$C_{48}H_{50}MgO_5S_2$	$C_{54}H_{94}MgO_7S_2$
fw	795.30	943.72
a (Å)	8.4785(4)	13.6755(2)
b (Å)	9.3595(5)	12.8045(6)
c (Å)	13.8306(6)	32.7127(12)
α (deg)	87.332(1)	90
β (deg)	85.929(1)	97.87(1)
γ (deg)	68.733(1)	90
V (Å$^{3)}$	1019.94(94)	5674.3(3)
Z	1	4
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
$d_{\mathrm{calc\ (g/cm^{3)}}}$	1.295	1.105
lin abs coeff (mm^{-1})	0.194	0.151
radiation	Mo Kα (0.710 73 Å)	Mo Kα (0.710 73 Å)
T (K)	150	150
R1, wR2 (all data)	0.1023, 0.1777	0.2005, 0.1774
R1, wR2 (>2σ)	0.0743, 0.1621	0.0909, 0.1397

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

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds **1** and **2**

[Mg(15-crown-5)(SCPh$_3$)$_2$],**1**

Mg(1)−S(1)	2.6607(8)	Mg(1)−O(4)	2.175(3)
Mg(1)−O(1)	2.187(3)	Mg(1)−O(5)	2.192(4)
Mg(1)−O(2)	2.143(3)	Mg(1)−O(3)	2.189(3)
S(1)−C(1)	1.864(3)	Mg(1)−S(1)−C(1)	126.03(10)
S(1)−Mg(1)−O(1)	88.02(12)		
S(1)−Mg(1)−O(2)	103.27(14)		
S(1)−Mg(1)−O(3)	79.50(15)		
S(1)−Mg(1)−O(4)	86.87(11)		
S(1)−Mg(1)−O(5)	92.7(2)		

[Mg(15-crown-5)(THF)$_2$][SMes*]$_2$, **2**

Mg(1)−O(1)	2.173(4)	Mg(1)−O(1S)	2.088(3)
Mg(1)−O(2)	2.195(4)	Mg(1)−O(2S)	2.098(3)
Mg(1)−O(3)	2.118(4)	S(1)−C(1)	1.769(5)
Mg(1)−O(4)	2.189(4)	S(2)−C(19)	1.780(5)
Mg(1)−O(5)	2.160(4)		
O(1S)−Mg(1)−O(1)	93.8(2)	O(2S)−Mg(1)−O(1)	87.7(2)
O(1S)−Mg(1)−O(2)	90.46(14)	O(2S)−Mg(1)−O(2)	93.43(14)
9O(1S)−Mg(1)−O(3)	90.5(2)	O(2S)−Mg(1)−O(3)	90.4(2)
O(1S)−Mg(1)−O(4)	90.44(14)	O(2S)−Mg(1)−O(4)	86.30(14)
O(1S)−Mg(1)−O(5)	86.01(14)	O(2S)−Mg(1)−O(5)	91.02(14)
O(1S)−Mg(1)−O(2S	176.1(2)		

thiol (eq 1) or (2) transamination involving the treatment of magnesium amide [Mg{N(SiMe$_3$)$_2$}$_2$]$_2$[15] with 4 equiv of thiol (eq 2).

$$(\text{n-Bu/s-Bu})_2\text{Mg} + 2\text{HSR} + \text{15-crown-5} \rightarrow \text{Mg(15-crown-5)(SR)}_2 + 2\text{n-Bu/s-BuH} \quad R = \text{CPh}_3, \text{2,4,6-tBu}_3\text{C}_6\text{H}_2 \qquad (1)$$

$$[\text{Mg}\{\text{N(SiMe}_3)_2\}_2]_2 + 4\text{HSR} + 2\ \text{15-crown-5} \rightarrow 2\text{Mg(15-crown-5)(SR)}_2 + 4\text{HN(SiMe}_3)_2 \quad R = \text{CPh}_3, \text{2,4,6-tBu}_3\text{C}_6\text{H}_2 \qquad (2)$$

Alkane elimination reactions, as employed in the synthesis for **1** and **2**, have been utilized previously to prepare a variety of magnesium derivatives.[10,11,13,15,20−22] Generally, the route proceeds smoothly, allowing a wide variety of ligands and solvents. In addition, the gaseous nature of the byproducts ensures an easy workup. However, the unavailability of dialkane derivatives of the heavier alkaline earth elements limits this sequence to the lighter alkaline earth derivatives.

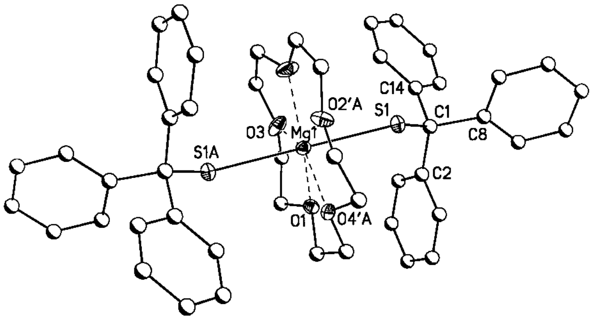

Figure 1. Computer generated plot of **1** with anisotropic displacement parameters depicting 30% probability for the non-carbon atoms. For clarity, carbon atoms are shown as standardized balls, and hydrogen atoms have been omitted.

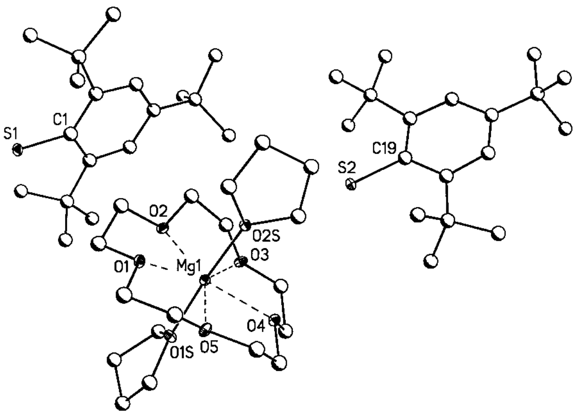

Figure 2. Computer generated plot of **2** with anisotropic displacement parameters depicting 30% probability for the non-carbon atoms. For clarity, carbon atoms are shown as standardized balls, and hydrogen atoms have been omitted.

Transamination has also been utilized for the synthesis of a wide variety of alkaline earth derivatives, such as thiolates,[10,13] selenolates,[10,23] tellurolates,[23,24] and phosphides.[25] A significant advantage of the transamination regime is, that it is applicable for all alkaline earth elements. Generally, the reactions proceed smoothly. If, however, a ligand of high acidity, such as a small, aromatic thiol, is utilized, care needs to be taken to avoid adding the acid too fast, since protonolysis of the liberated secondary amine, under formation of primary amine, and consequently ammonia, or an ammonium salt may be observed.[26]

Crystallographic information and data collection parameters for compounds **1** and **2** are summarized in Table 1 and the Experimental Section. A compilation of pertinent bond distances and angles for the compounds is given in Table 2, while Figures1 and 2 illustrate the structural principles displayed in compounds **1** and **2**, respectively. In each complex, geometrical data for the respective crown ether molecule (bond distances and angles) were unexceptional and can be found in greater detail in the deposited crystallographic data.

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Table 3. Comparison of Some Structural Features in Magnesium Thiolates[a]

compd	coord no.	Mg−S (Å)	donor	Mg−donor (Å)	ref
$[\mathrm{Mg(STriph)_2}]_2$	3+ar	2.35 2.46^{br}	ar	2.56, 2.80	10
$[\mathrm{Mg(Tp^{\mathit{p}-Tol})SH}]$	4	2.35	−	−	11
$\mathrm{Mg(SMes^*)_2(Et_2O)_2}$	4	2.39	$\mathrm{Et_{2O}}$	2.07	10
$[\mathrm{Mg(THF)(SMes^*)_2}]_2$	4	2.37 2.51^{br}	THF	2.03	33
$[\mathrm{(CuMes)_4(\mu\text{-}SAr)_2(MgSAr)_2}]$	4	2.38 2.43^{br}	$\mathrm{N^a}$	2.18	9
$\mathrm{Mg(HMPA)_2(SSiPh_3)}$	4	2.43	HMPA	1.94	29
$[\mathrm{(C_7H_9NH)}]_2[\mathrm{Mg(SC_6F_5)_4}]$	4	2.45	−	−	13
$[\mathrm{Mg(SC_6H_4\text{-}2\text{-}CH_2NMe_2)_2}]_2$	5	2.45 2.55^{br}	$\mathrm{N^a}$	2.25	12
$\mathrm{Mg(S\text{-}2NC_5H_4)_2(py)_2}$	6	2.61	$\mathrm{N^a}$	2.19	13
$[\mathrm{Mg_3(\eta^2SPh)_6(py)_6}]$	6	2.61	py	2.22	13
$\mathrm{Mg(SPh)_2(py)_4}$	6	2.63	py	2.29	13
$\mathrm{Mg(SC_6F_5)_2(py)_4}$	6	2.65	py	2.28	29
$\mathrm{Mg(15\text{-}C\text{-}5)(SCPh_3)_2}$	7	2.66	15-crown-5	2.14−2.19	*b*
$[\mathrm{Mg(15\text{-}C\text{-}5)(THF)_2}][\mathrm{SMes^*}]_2$	7	−	15-crown-5 THF	2.09−2.20 2.09	*b*

[a] Abbreviations: ar = arene; br = bridging; a = intermolecular interaction; HMPA = hexamethylphosphoramide, py = pyridine. [b] This work.

[Mg(15-crown-5)($\mathrm{SCPh_3}$)$_2$], 1. Compound **1** is shown in Figure 1, selected bond lengths and angles are presented in Table 2. Mg(1) resides over a crystallographic inversion center, such that the two thiolate ligands are equivalent and exhibit a required 180° S(1)−Mg(1)−S(1A) bond angle. The remainder of the coordination environment about the seven-coordinate cation is occupied by five crown ether oxygen atoms. The Mg(1)−S(1) bond distance is 2.6607(8) Å, and the Mg(1)−O distances occur over a range of 2.143(3)−2.192(4) Å. The trityl thiolate ($\mathrm{CPh_3}$) ligand is oriented essentially perpendicular to the crown plane with S(1)−Mg(1)−O angles ranging over 76.73(14)−103.27(14)°. With respect to the thiolate ligand, the Mg(1)−S(1)−C(1) angle is 126.03(10)°, and the S(1)−C(1) bond distance is 1.864(3) Å. The phenyl rings are oriented about C(1) in a tetrahedral fashion; the geometrical data for the phenyl groups and crown ether are unremarkable.

[Mg(15-crown-5)(THF)$_2$][SMes*]$_2$, 2. Compound **2**, displayed in Figure 2, shows Mg(1) to be formally seven-coordinate with no contact to either of the two thiolate anions (distance > 5 Å). The crown ether is connected to Mg(1) between 2.118(4) and 2.195(4) Å; completing the coordination environment about the cation are two THF molecules oriented trans to one another at 2.088(3) and 2.098(3) Å from Mg(1). The O(1S)−Mg(1)−O(2S) bond angle is essentially linear at 176.1(2)°, and the range of THF−Mg(1)−O(crown) bond angles is close to orthogonal at 86.01(14)−93.8(2)°. With respect to the thiolate anions, the $\mathrm{S{-}C_{ipso}}$ bond distances are 1.796(5) Å for S(1)−C(1) and 1.780(5) Å for S(2)−C(19). Remaining geometrical data for the arylthiolates and crown ether are unremarkable.

Discussion

The existence of contact and separated ions was first described in 1958[27] and has since been most intensively investigated for organometallic alkali derivatives.[28] During our investigations into the coordination chemistry of alkaline earth metal chalcogenolates, it became evident that separated ions are commonly formed, typically associated with a dramatic change in physical properties, such as solubility or volatility. These altered physical properties greatly affect their use as precursor materials and synthetic reagents, and illuminate new avenues in the cleanup of hazardous waste materials. This investigation is now examining factors determining variables responsible for the formation of the contact or separated alkaline earth chalcogenolates. We here present two magnesium derivatives, where the variation of ligand size allowed the successive formation of contact versus separated ion triplets.

Over the past decade about two dozen well-characterized magnesium chalcogenolates have been reported.[9−13,22−24] Among those, one separated species, [Mg(12-crown-4)$_2$][$\mathrm{TeSi(SiMe_3)_3}$]$_2$ has been mentioned;[23] however, no structural data are available, and its separated nature was deducted from conductivity experiments. All other compounds display bonding interactions between cation and anions.

Compound **1** displays a seven-coordinate magnesium center, which is on the upper end of coordination numbers observed for magnesium chalcogenolates (Table 3). Nevertheless, the Mg−S bond length (2.66 Å) is only slightly longer than that for the six-coordinate analogues, indicating the relatively small size of the trityl thiolate ligand. In fact, the almost planar crown ether conformation ensures the location of all donor atoms in the equatorial plane about the metal, resulting in a space requirement that is comparable to the four equatorial pyridine donors in the six-coordinate $\mathrm{Mg(SPh)_2(py)_4}$[13] or $\mathrm{Mg(SC_6F_5)_2(py)_4}$.[29]

Utilization of a ligand with increased steric requirement results in the separation of metal and ligands. Compound **2** is the first structurally characterized separated magnesium chalcogenolate. The magnesium center is seven-coordinate with 15-crown-5 and THF completing its coordination sphere. The metal coordination in **1** and **2** is very similar: in **1** two $-\mathrm{SCPh_3}$ ligands occupy the axial coordination sites; in **2**, THF fills these positions. Apparently, the conformation of the crown ether prohibits the close approach of the sterically demanding HSMes* ligand. The formation of the separated species is indicative of steric repulsion between the crown ether and the *o*-tBu substituents on the ligands, thus favoring Mg−THF coordination. Similar results were observed for potassium thiolates, where changing the crown ether (dibenzo-18-crown-6 versus 18-crown-6) resulted in the formation of either contact or separated ion pairs.[30] Utilization of dibenzo-18-crown-6 resulted in the formation of the contact pair [K(dibenzo-18-crown-6)SMes*].

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(27) Winstein, S.; Robinson, G. C. *J. Am. Chem. Soc.*, **1958**, *80*, 169.

(28) See for example: Weiss, E. *Angew. Chem., Int. Ed. Engl*. **1993**, *32*, 1501, and references cited therein.

(29) Chadwick, S.; Teng, W.; Englich, U.; Ruhlandt-Senge, K. Unpublished results.

The dibenzo crown adopts a cup-shaped arrangement, creating a void where the bulky anion can approach the metal center. In contrast, and very similar to the magnesium thiolates **1** and **2**, 18-crown-6 adopts a planar conformation, preventing the approach of the sterically encumbered SMes* ligand. Accordingly, the cation completes its coordination sphere with two additional THF donors, resulting in [K(18-crown-6)(THF)$_2$]-[SMes*].[30] If the smaller trityl thiolate is used, a contact pair, [K(18-crown-6)SCPh$_3$], is formed,[31] indicating a very comparable trend, as observed for compounds **1** and **2**.

Comparing **2** to [Mg(12-crown-4)$_2$][TeSi(SiMe$_3$)$_3$]$_2$[23] sheds light into an additional aspect of the formation of contact versus separated species: the formation of the separated tellurolate is not only a consequence of steric influence but also of the small magnesium−tellurium bond strength − a result of reduced charge density and inefficient orbital overlap.[32] This argument is further supported by the lack of separated phenolate or alkoxide species, where the high charge density on the ligand atom results in considerable metal−ligand bond strength and high reactivity of the separated phenolate or alkoxide anion. Moreover, the small size difference between the metal and ligand orbitals ensures an effective orbital overlap. Consequently, the formation of contact versus separated species is an indirect measure of magnesium−ligand bond strength.

Conclusions

The directed synthesis of magnesium thiolates displaying either magnesium−sulfur contacts or a coordination sphere occupied solely by Lewis donors is an important step in the development of precursor materials for group IIB−VIA semiconductor technology. Since the ionic association of the target compounds coincides with significant changes in physical properties, a detailed analysis of structure determining factors is warranted. As shown here, small changes in ligand size have a dramatic effect on the ionic association in the solid state. Our work continues to further evaluate structure−function relationships in alkaline earth derivatives.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) Chadwick, S.; Englich, U.; Ruhlandt-Senge, K. *Organometallics* **1997**, *16*, 5792.

(32) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999.