Syntheses and Structures of Magnesium Pyridine Thiolates—Model Compounds for Magnesium Binding in Photosystem I

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Abstract: Novel magnesium pyridine-2-thiolates were prepared by using alkane elimination chemistry. The resulting complexes display a metal coordination environment composed of sulfur/nitrogen bonding from the intramolecularly stabilized mercaptopyridine ligand, in addition to coordination by the oxygen centers from two THF donors. The compounds are well-suited model compounds for the magnesium centers in Photosystem I, in which magnesium, situated in the central chlorophyll ligand, is bound to sulfur from a nearby methionine residue. All compounds were characterized by ^{1}H, ^{13}C NMR, and IR spectroscopy, in addition to X-ray crystallography.

Keywords: biomimetic model compounds · magnesium · N ligands · Photosystem I · S ligands

Introduction

The recent structure elucidation of Photosystem I to 2.5 Å resolution revealed some remarkable surprises.[1] One of the most unexpected results was the coordination environment of the magnesium ion situated at the center of the chlorophyll that serves as the primary acceptor of electrons in the photosystem. This magnesium center is coordinated to four nitrogen atoms from the chlorophyll chromophore, in addition to a sulfur atom from a nearby methionine residue, making this the first structurally authenticated example of magnesium–sulfur binding in nature. This remarkable structural element is especially surprising since it was commonly believed that a soft sulfur atom would not interact favorably with the small, hard magnesium atom. Rather, magnesium would bind preferentially to small, hard ligand systems with oxygen or nitrogen functionalities.[2]

So far, only few magnesium complexes with sulfur and nitrogen coordination have been reported, resulting in very few species available for direct comparison with the magnesium site in Photosystem I. Remarkably, none of these compounds sheds light on the binding of nitrogen and sulfur to magnesium, as found in Photosystem I.

The main structure-determining factor among magnesium thiolates is the steric bulk of the thiolate ligand.[3] Employment of sterically very cumbersome ligands enables the isolation of compounds with low coordination numbers, as observed in the pseudo two-coordinate $[Mg(S\text{-}2,6\text{-}Trip_2C_6H_3)_2]$ (Trip = $2,4,6\text{-}i\text{Pr}_3C_6H_2$),[4] or pseudo three-coordinate $[Mg(STriph)(\mu_2\text{-}STriph)]_2$ (Triph = $2,4,6\text{-}Ph_3C_6H_2$).[5] Both compounds display arene interactions between the *ortho* substituents of the ligand and the metal center. Sterically demanding ligands are also needed to allow the isolation of compounds with a coordination number of four, as evidenced by $[Mg(Et_2O)_2(SMes^*)_2]$ (Mes* = $2,4,6\text{-}t\text{Bu}_3C_6H_2$),[5] $[Mg(Tp^{p\text{-tol}})SH]$ ($Tp^{p\text{-tol}}$ = tris(3-*p*-tolylprazolyl)hydroborate),[6] and others (see Table 1). If smaller ligands are utilized, compounds with coordination numbers of five or higher are observed.[3]

Model compounds for comparison with the magnesium center in Photosystem I require magnesium derivatives with ambivalent sulfur and nitrogen binding ligands. So far, only a few magnesium thiolates with additional nitrogen coordination have been disseminated, including the five-coordinate $[Mg(SC_6F_5)_2(py)_3]$,[7] and the six-coordinate $[Mg(SPh)_2(py)_4]$,[7] and $[Mg_3(\mu_2\text{-}SPh)_6(py)_6]$.[7] Examples of compounds in which the nitrogen donation is achieved by intramolecular coordination include the heteroorganocuprate $[Mg_2(SC_6H_4\text{-}((R)\text{-}CH(Me)NMe_2))_4Cu_4(Mes)_4]$ (Mes = $2,4,6\text{-}Me_3C_6H_2$,[8] and the five-coordinate dimer $[Mg(SC_6H_4\text{-}2\text{-}CH_2NMe_2)_2]_2$.[9] No example is available in which sulfur acts as a Lewis donor. The only compounds in which an ambivalent ligand system has been employed are a group of magnesium derivatives with sulfur and nitrogen coordination, prepared by insertion of isothiocyanate into a Mg–C bond of a diorganomagnesium derivative. Examples include $[Mg(thf)_2(SCPhNt\text{Bu})_2]$,[10]

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Table 1. Selected geometrical details for compounds **1**–**4** and related compounds.

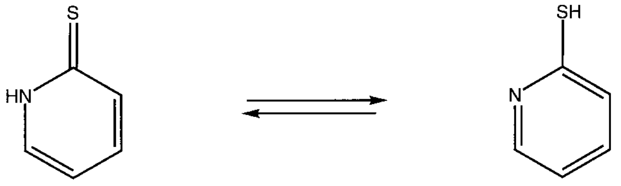
Compound	CN[a]	Mg–S [Å]	Mg–N [Å]	D	Mg–D [Å]	Ref.
$[Mg(thf)_2\{N(SiMe_3)_2\}(SMes^*)]$	4	2.431(2)	1.998(3)	THF	2.042(3)	[16]
$[\{Mg(thf)\{N(SiMe_3)_2\}(SPh)\}_2]$	4	2.522(2), 2.533(2)	2.001(3)	THF	2.028(3)	[16]
$[AlMe_2Al(\mu\text{-}i Pr_2N)_2Mg(t BuN)(CH_3S)]$	4	2.429(2)	2.150(4)	$N(i Pr)_2$	2.132(6), 2.148(6)	[11]
$[\{Mg(thf)(N(SiMe_3)_2)(S\text{-}2,4,6\text{-}i Pr_3C_6H_2)\}_2]$	4	2.4978(5), 2.5321(5)	2.001(1)	THF	2.050(1)	[16]
$[Mg(thf)_2\{N(SiMe_3)_2\}_2]$	4	–	2.015(5), 2.027(5)	THF	2.033(5), 2.048(5)	[15]
$[Mg(py)_3(SC_6F_5)_2]$	5	2.470(2), 2.481(2)	–	py	2.18(1) av	[7]
$[\{Mg(SC_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}_2]$	5	2.549(4) (av),[b] 2.446(2)[c]		NMe_2	2.252(3) av, 2.239(4)	[9]
$[Mg(thf)_2(SCPhNt Bu)_2]$	6	2.584(2)	2.176(5)	THF	2.230(4)	[10]
$[Mg(thf)_2\{SC(NPh)Ni Pr_2\}]$	6	2.5595(13)	2.112(2)	THF	2.191(2)	[10]
$[Mg_2(OEt_2)_2(SCEtNPh)_4]$	6	2.535(3), 2.690(3) ,2.657(3)	2.138(6), 2.185(6)	OEt_2	2.099(6)	[10]
$[Mg(py)_2(pyS)_2]$	6	2.62(1) (av)		N(ligand)[b]	2.149(3) av	[7]
				py	2.246(3) av[d]	
$[Mg(thf)_2(pyS)_2]$	6	2.604(1)		N(ligand)[b]	2.137(1)	this work
				THF	2.103(2)	
$[Mg(thf)_2(3\text{-}CF_3\text{-}pyS)_2]$	6	2.584(2)		N(ligand)[b]	2.159(4)	this work
				THF	2.078(3)	
$[Mg(thf)_2(5\text{-}CF_3\text{-}pyS)_2]$	6	2.6072(4)		N(ligand)[b]	2.153(1)	this work
				THF	2.066(1)	
$[Mg(thf)_2(3\text{-}SiMe_3\text{-}pyS)_2]$	6	2.576(3)		N(ligand)[b]	2.143(1)	this work
				THF	2.093(6)	
$[Mg(py)_4(SPh)_2]$	6	2.6247(5)		py	2.220(2), 2.360(2)	[7]

[a] CN = coordination number. [b] Bridging. [c] Terminal. [d] Due to disorder a significant uncertainty about ligand and donor positions exist.

$[Mg(thf)_2\{SC(NPh)Ni Pr_2\}_2]$,[10] the dimeric $[Mg_2(OEt_2)_2(SCEtNPh)_4]$,[10] and the polynuclear $[AlMe_2(\mu\text{-}i Pr_2N)_2Mg(t BuNCH_3S)]$.[11] An additional example is the six-coordinate mercaptopyridine derivative $[Mg(py)_2(pyS)_2]$.[7] However, significant disorder in the last example, due to statistically distributed donors and ligands, make the structure determination of this compound less than ideal.

As a consequence, few compounds are available to mimic the metal environment in Photosystem I and allow for the analysis of metal binding to nitrogen and sulfur. To illuminate which element would bind favorably as a ligand or donor to the magnesium center, a ligand system in which either sulfur or nitrogen can act as a donor or ligand is needed.

The mercaptopyridine ligand displays two tautomeric forms (Scheme 1): a thiol and an α-thione.[12] Interestingly, the α-thione form is predominant in the crystal, indicating that the drive towards aromatization does not predetermine which of the two donor atoms would bind preferentially to the metal atom. Accordingly, this ligand is ideally suited for model compounds of Photosystem I, since it will indicate if magnesium will preferentially bind to sulfur or nitrogen; if a magnesium–nitrogen interaction is favored over a magnesium–sulfur bond, one would expect the α-thione form to be precedent. In this case short, strong magnesium–nitrogen amide-type bonds, and long, weak metal–sulfur bonds with increased C–S bond order would be observed. In case of a substantial magnesium–sulfur contact, the thiolate form of the ligand would be favored and nitrogen atom would act as a Lewis donor.



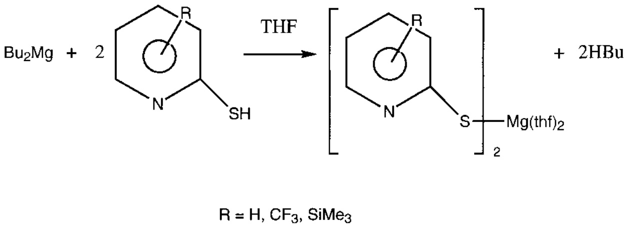
Scheme 1. The two tautomeric forms of the mercaptopyridine ligand.

Here we report on a family of magnesium compounds bearing a bidentate ligand system with sulfur and nitrogen functionalities, achieved through the pyridine function in the mercaptopyridine ligand. The compounds presented include $[Mg(thf)_2(pyS)_2]\cdot 0.5\,THF$ (**1**), $[Mg(thf)_2(3\text{-}CF_3\text{-}pyS)_2]$ (**2**), $[Mg(thf)_2(5\text{-}CF_3\text{-}pyS)_2]$ (**3**), and $[Mg(thf)_2(3\text{-}SiMe_3\text{-}pyS)_2]\cdot 0.5\,THF$ (**4**). The coordination environment about magnesium will give important insight into magnesium–sulfur and magnesium–nitrogen binding in the target molecules, and thus in Photosystem I. Four different substitution patterns on the mercaptopyridine ligands will shed light on the effect of ligand bulk on the metal environment. Moreover, the role of CF_3 and $SiMe_3$ substitution on the mercaptopyridine ligand to modulate solubility will be explored.

Results

Synthetic aspects: Compounds **1**–**4** were synthesized in a straightforward manner by alkane elimination involving the treatment of $Mg(C_4H_9)_2$ with the different mercaptopyridine ligands in THF, as shown in Scheme 2.

The reaction of dibutyl magnesium with chalcogenols has been used previously for the preparation of magnesium



Scheme 2. The preparation of compounds **1**–**4** by alkane elimination.

chalcogenolates bearing a wide variety of ligands and donors. The products are generally isolated in excellent yield and purity, indicating the high synthetic potential of this reaction scheme.[5, 7, 13]

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. NMR spectral analysis of the vacuum dried crystals confirmed the identity of all compounds. In compounds **2**–**4** the overall formula $[Mg(thf)_2L_2]$, in which L is the corresponding thiolate ligand, was confirmed. Compound **1** contains less than the two and one half equivalents of THF, as predicted by X-ray crystallography. Reproducibly, THF is lost upon drying the sample in vacuum, coinciding with the loss of crystallinity.

The solubility of the target compounds in nondonating solvents is very limited, indicating the polymeric nature of the unsolvated species. Addition of donor solvents such as pyridine or THF affords clear solutions, presumably the result of the break-up of metal–chalcogen bridges that form the polymer in favor of metal–donor interactions, resulting in discrete molecules with enhanced solubility. The $-CF_3$ and $-SiMe_3$ substitution of the ligand, as compared with the unsubstituted mercaptopyridine, results in a dramatic increase of solubility. While $-SiMe_3$ substitution increases the lipophilicity, $-CF_3$ substitution is responsible for an increase in electrostatic repulsion that affects solubility by the weakening of the metal–chalcogen interactions that build the polymer.

Structural aspects: The structures of the four complexes are very similar and will be described together. Compound **3** is shown in Figure 1, while compound **4** is presented in Figure 2. An illustration of compound **2** is provided in the Tabble of Contents.

Complexes **1**–**4** consist of discrete molecules in which the magnesium atom is hexacoordinate with the nitrogen and sulfur atoms of the two mercaptopyridine ligands, which act as chelating ligands. Also coordinated to the magnesium centers are two THF donors. The magnesium atom is in a distorted octahedral environment, and in all cases, the narrow N-Mg-S ligand bite angle (65.81(4) to 66.45(10)°) is the main source of the distortion. The mercaptopyridine ligands are arranged in a conformation in which the sulfur atoms are *trans* with respect to one another. The nitrogen atoms of the ligands are also arranged *trans* with respect to the metal-bound oxygen atoms of the THF donors. The bond angles between the *trans*-positioned donor atoms (N-Mg-O) range from 156.53(3) to 163.65(14)°. The Mg–S, Mg–N, Mg–O bond lengths are found in the ranges 2.5695(9)–2.6079(6), 2.1410(4)–2.169(1), and 2.066(1) to 2.117(1) Å, respectively. The geometric parameters for the aromatic rings, particular the N–Cα distances, and the THF units are typical and will not be discussed in detail.

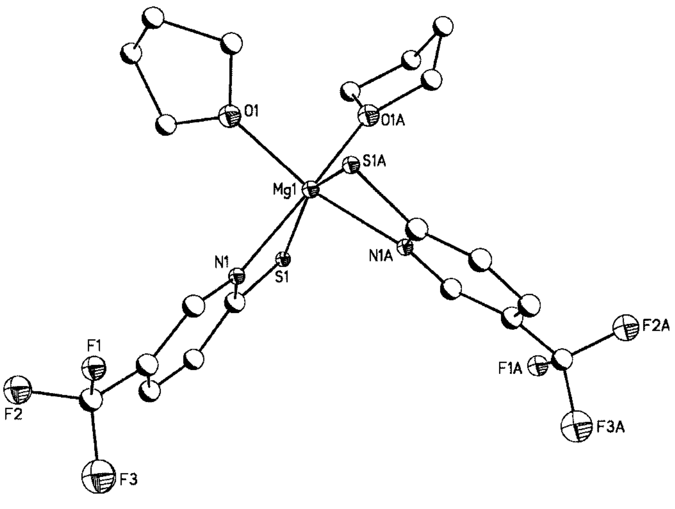


Figure 1. Computer generated plot of **3** with anisotropic displacement parameters depicting 30% probability. The hydrogen atoms have been omitted for clarity.

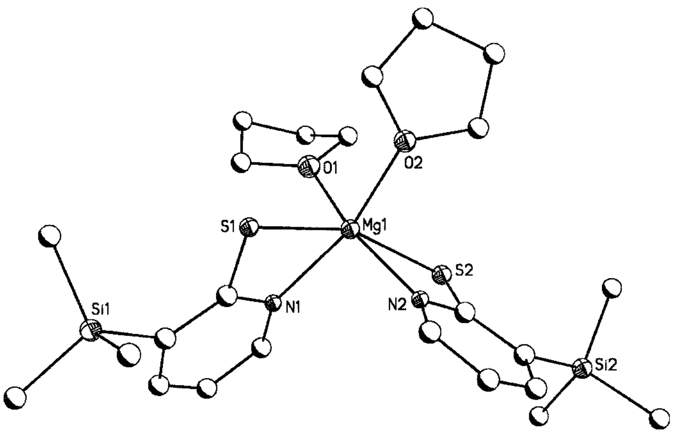


Figure 2. Computer generated plot of **4** with anisotropic displacement parameters depicting 30% probability. The hydrogen atoms have been omitted for clarity.

Discussion

The main motivation for this work was to investigate the nature of the magnesium–nitrogen and magnesium–sulfur interactions observed crystallographically in Photosystem I,[1] by utilizing a ligand that provides both nitrogen and sulfur coordination. In the mercaptopyridine system nitrogen and sulfur can both act as either donors or ligands, since the two tautomeric forms of the ligand allow both possibilities (see Scheme 1).[12] To shed light onto the unexpected magnesium binding detected in Photosystem I,[1] it is necessary to explore if the small, hard magnesium would preferably interact with the nitrogen in the ligand and display short metal–nitrogen distances, and long, weak sulfur interactions; or if the metal–sulfur contacts would lie in the range of previously observed magnesium–thiolate distances, coinciding with long metal–nitrogen donor interactions. Precedence for both scenarios has been observed in a series of alkali metal mercaptopyridine derivatives in which the lithium derivative $[(LipyS)_2[18]\text{-crown-}6]$ displayed unusually long Li–S and very short Li–N bonds, interpreted as amide type bonds through the α-thione form of the ligand.[14] In contrast, the heavier alkali metal derivatives display relatively short metal–sulfur distances, coinciding with a relative increase in metal–nitrogen bond lengths. This arrangement was made possible through the thiolate form of the ligand.[14] The ambivalent nature of the ligand in terms of metal binding can be interpreted as a manifestation of the hard–acid/hard–base paring between the alkali metal and the nitrogen and sulfur centers in the resonance delocalized anion.[15]

The metal coordination in **1**–**4** and the six-coordinate thiolate [$Mg(py)_4(SPh)_2$][7] is very similar, with the magnesium center connected to two sulfur, two nitrogen, and two oxygen atoms. Since the space requirement of the separate phenylthiol and pyridine in the last compound is higher than that in the intramoleculary coordinated **1**–**4**, the magnesium–thiolate bond lengths in [$Mg(py)_4(SPh)_2$] are expected to be elongated. In contrast, the Mg–S and Mg–N bond lengths in **1**–**4**, the six-coordinate bidentate [$Mg(thf)_2(SCPhN\textit{t}Bu)_2$],[10] [$Mg(thf)_2\{SC(NPh)N\textit{i}Pr_2\}_2$],[10] and the dimeric [$Mg_2(OEt_2)_2(SCEtNPh)_4$][10]] should be very similar. Indeed, the metal–sulfur bonds in **1**–**4**, observed in a narrow range between 2.576(3) Å and 2.6072(4) Å, are in good agreement with the bidentate derivatives, but are slightly shorter than those in [$Mg(py)_4(SPh)_2$] (2.6247(5) Å), thus reflecting the influence of reduced steric bulk on the metal–ligand bond length. The reduced steric demand that the bidentate ligands provide in **1**–**4** is expressed by the narrow N-Mg-S bite angles (65.71(4) to 66.45(10)°) and significant deviation from regular octahedral geometry. Not surprisingly, the Mg–S bond lengths in **1**–**4** are in the same range as those in [$Mg(py)_2(pyS)_2$] (2.62(1) Å),[7] and also compare favorably with the bridging metal–sulfur distances in the five-coordinate intramolecular stabilized [$\{Mg(SC_6H_4\text{-}2\text{-}CH_2NMe_2)_2\}_2$] (2.548(2) Å).[9] The Mg–S distances in **1**–**4** also agree well with the sum of radii for six-coordinate Mg^{2+} and S^{2-} (2.56 Å),[16] classifying the magnesium–sulfur distance in **1**–**4** as magnesium–thiolate interactions with significant ionic contribution.

This view is further supported by comparing the Mg–N(ligand) distances in **1**–**4** (2.15 Å (av)) with the previously reported [$Mg(py)_2(pyS)_2$] (2.149(3) Å),[7] the five-coordinate [$Mg(py)_3(SC_6F_5)_2$] (2.18 Å (av)),[7] the six-coordinate [$Mg(py)_4(SPh)_2$] (2.22 Å (av)),[7] and [$Mg_3(py)_6(\mu_2\text{-}SPh)_6$] (2.22 Å (av)),[7] and the intramoleculary coordinated [$Mg(thf)_2(SCPhN\textit{t}Bu)_2$] (2.176(5) Å),[10] [$Mg(thf)_2\{SC(NPh)N\textit{i}Pr_2\}_2$] (2.112(2) Å),[10] and [$Mg_2(OEt_2)_2(SCEtNPh)_4$] (2.138(6) and 2.185(6) Å).[10] This excellent agreement, and the significantly shorter Mg–N distances in the four-coordinate magnesium amide [$Mg(thf)_2(N(SiMe_3)_2)_2$] (2.02 Å (av)),[15] indicate that an amido contribution in the mercaptopyridine derivatives **1**–**4** is not likely. This leads to an interpretation of magnesium binding in the mercaptopyridine ligand that the sulfur acts as a ligand and nitrogen as a Lewis donor. Comparison of **1**–**4** with heteroleptic magnesium amide thiolates, such as the four-coordinate monomeric [$Mg(thf)_2N(SiMe_3)_2SMes^*$] (Mg–S 2.431(2) Å, Mg–N 1.998(3) Å), or the dimeric five-coordinate [$\{Mg(OEt_2)_2N(SiMe_3)_2(Strip)\}_2$] with a bridging Mg–S functionality (Mg–S 2.4978(5), 2.5321(5) Å; Mg–N 2.001(1), 2.050(1) Å)[18] further supports this view. Despite lower coordination numbers, the Mg–S bond lengths compare well, while the Mg–N distances in **1**–**4** are significantly longer, indicating that the Mg–N contacts in **1**–**4** are based on Lewis donor interactions.

Finally, the view of magnesium–thiolate bonding and nitrogen acting as a Lewis donor (thiol form of the ligand) is also confirmed by analyzing the S–C distances in **1**–**4**. If the ligand binds as a thiolate, an S–C single bond is expected. If a significant metal–amido contribution existed, the α-thiopyridone form of the ligand would be prevalent, coinciding with an increase in S–C bond order, and weak, long Mg–S bonds (see Scheme 1). The S–C distances in **1**–**4** are observed in a narrow range at 1.738(3) Å (av) for **1**, 1.733(4) Å (av) for **2**, 1.732(1) Å for **3**, and 1.753(8) Å (av) for **4**. These numbers compare well with the S–C distances in [$Mg(py)_2(pyS)_2$] (1.763(3) and 1.748(3) Å),[7] and a number of alkali metal mercaptopyridine derivatives such as [Na([15]crown-5)(pyS)] (1.735(3) Å),[14] or the polymeric [$\{K(\mu\text{-}pyS)_2([15]crown\text{-}5)\}_n$] (1.735(5) and 1.750(5) Å).[14] In contrast, the S–C bond length in free neutral α-thiopyridone is significantly shorter (1.68(2) Å), indicating the multiple bond character of the S–C bond.[12] This indicates that the drive towards aromatization is not structure determining, rather the preferred metal–ligand interaction will influence the form of the ligand.

The narrow range of Mg–S bond lengths in **1**–**4** suggests the small influence of CF_3 and $SiMe_3$ substitution on the overall structural outcome. However, both $SiMe_3$ and CF_3 substituents have a major influence on solubility, but apparently not on the expense of additional crowding of the metal center.

Conclusion

Compounds **1**–**4** have been prepared using an intramolecularly coordinating mercaptopyridine ligand to investigate the magnesium–nitrogen and magnesium–sulfur binding, as recently observed in Photosystem I. The mercaptopyridine ligand possesses two tautomeric forms, a thiol and an α-thiopyridone to enable both the sulfur and nitrogen to bind either as a ligand or a donor. In compounds **1**–**4**, the sulfur was identified to bind through the thiolate form of the ligand, with the nitrogen acting as a Lewis donor, indicating the propensity of magnesium to bind thermodynamically favorably to sulfur.

Experimental Section

General procedures: All reactions were performed under a purified argon atmosphere by using modified Schlenk techniques and/or a Braun Labmaster 100 dry box. *n*-Hexanes, and tetrahydrofuran (THF) were distilled just prior to use from a Na/K alloy followed by two freeze-pump-thaw cycles. Dibutylmagnesium (1M solution of a statistical mixture of *n*- and *sec*-butyl magnesium ($(n\text{Bu}/s\text{Bu})_2Mg$ in heptane) was obtained from a commercial source and used as received. Commercially available pySH, 3-CF_3-pySH, and 5-CF_3-pySH were purified by recrystallization from diethyl ether. 3-$SiMe_3$-pySH was prepared by published procedures.[19] ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 spectrometer. Spectra were recorded in C_6D_6 and referenced to residual solvent resonances. IR spectra were recorded as Nujol mulls between NaBr plates on a Perkin–Elmer PE 1600 FI-IR spectrometer. Melting points are uncorrected. Reliable elemental analyses could not be obtained, even when glove-box handling was attempted, due to the high moisture and oxygen sensitivity of all compounds reported. In addition, a too low carbon content is commonly obtained, due to the formation of nonvolatile carbonates. This is a well-known problem in alkaline earth metal chemistry.[20]

General procedure for the preparation of compounds 1–4: A 100 mL Schlenk tube was flame-dried three times under vacuum and, under an argon atmosphere, charged with the corresponding thiol (2 mmol). The thiol was dissolved in dry THF (25 mL). Bu_2Mg (1 mL, 1 mmol) was added dropwise to the reaction mixture by syringe. The resulting solution was stirred for 30 minutes and, in each case, became clear. Dry hexane was added dropwise by cannula to the reaction mixture, until a light turbidity was observed. This was followed by the dropwise addition of THF until the precipitate had redissolved, upon which the sample was placed in a freezer (−20 °C). In each case this technique gave pale yellow single crystals suitable for study by X-ray diffraction. Yields are not optimized.

[Mg(pyS)$_2$(thf)$_2$]·0.5THF (1): ^{1}H NMR (C_6D_6): $\delta = 7.33$ (s, 2H), 6.50 (s, 2H), 6.26 (s, 2H), 5.53 (s, 2H), 3.61 (br m, 2H; THF), 1.41 ppm (br m, 2H; THF); ^{13}C NMR (C_6D_6): $\delta = 137.04$, 68.45, 26.04 ppm; IR (KBr plates, Nujol mull): $\tilde{\nu} = 2923.0$ (s), 2853.5 (s), 1613.8 (w), 1587.3 (m), 1558.3 (w), 1521.1 (w), 1506.2 (w), 1496.0 (w), 1456.3 (m), 1415.9 (m), 1366.8 (w), 1258.3 (w), 1181.2 (w), 1138.8 (s), 1103.0 (w), 1085.3 (w), 1041.4 (w), 984.0 (w), 903.8 (w), 869.4 (w), 801.9 (w), 744.0 (w), 728.3 cm^{-1} (w); m.p. 132 °C (decomp); yield: 0.13 g, 0.31 mmol, 31 %.

[Mg(3-CF$_3$-pyS)$_2$(thf)$_2$] (2): ^{1}H NMR (C_6D_6): $\delta = 7.90$ (s, 2H), 5.87 (s, 4H), 3.66 (br m, 16H; THF), 1.17 ppm (br m, 16H; THF); ^{13}C NMR (C_6D_6): $\delta = 136.00$, 114.37, 69.51, 25.50 ppm; IR (KBr plates, Nujol mull): $\tilde{\nu} = 2922.3$ (s), 2852.7 (s), 1588.4 (s), 1551.8 (s), 1461.7 (s), 1395.1 (s), 1319.9 (s), 1246.0 (w), 1198.0 (m), 1134.9 (s), 1101.5 (s), 1067.2 (s), 917.0 (w), 881.1 (m), 808.3 (m), 752.3 (m), 720.0 (m), 662.4 (w), 582.2 cm^{-1} (w); m.p. 177 °C (decomp); yield: 0.16 g, 0.031 mmol, 30.5 %.

[Mg(5-CF$_3$-pyS)$_2$(thf)$_2$] (3): ^{1}H NMR (C_6D_6): $\delta = 8.22$ (s, 2H), 7.26 (2H), 6.72 (s, 2H), 3.61 (br m, 8H; THF), 1.17 ppm (br m, 8H; THF); ^{13}C NMR (C_6D_6): $\delta = 133.19$, 122.75, 69.41, 25.55 ppm; IR (KBr plates, Nujol mull): $\tilde{\nu} = 2925.8$ (s), 2852.8 (s), 1608.5 (s), 1539.9 (s), 1461.7 (s), 1380.5 (m), 1360.4 (m), 1325.2 (s), 1273.0 (s), 1231.9 (s), 1147.2 (s), 1107.2 (s), 1071.8 (s), 1028.4 (s), 114.9 (s), 988.4 (w), 940.4 (w), 918.7 (w), 880.2 (s), 840.3 (s), 792.9 (w), 746.1 (w), 678.5 (w), 660.0 cm^{-1} (w); m.p. 167 °C (decomp); yield: 0.29 g, 0.55 mmol, 55 %.

[Mg(3-SiMe$_3$-pyS)$_2$(thf)$_2$]·0.5THF (4): ^{1}H NMR (C_6D_6): $\delta = 7.90$ (s, 2H), 7.25 (s, 2H), 6.23 (s, 2H), 3.69 (br m, 8H; THF), 1.25 (br m, 8H; THF), 0.64 ppm (s, 18H, SiMe3); ^{13}C NMR (C_6D_6): $\delta = 143.80$, 115.61, 69.14, 25.67, −0.60 ppm; IR (KBr plates, Nujol mull): $\tilde{\nu} = 2916.3$ (s), 2854.3 (s), 1570.4 (w), 1534.9 (m), 1458.4 (s), 1375.7 (m), 1361.5 (s), 1310.5 (w), 1238.6 (m), 1219.5 (w), 1135.9 (m), 1070.4 (w), 1035.6 (m), 917.7 (w), 880.0 (w), 839.5 (s), 798.4 (w), 764.7 (m), 748.4 (w), 722.3 (w), 686.6 (w), 674.1 (w), 622.2 cm^{-1} (w); m.p. 128 °C (decomp); yield: 0.36 g, 0.61 mmol, 62 %.

X-ray crystallographic studies: X-ray quality crystals for all compounds were grown as described above. 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 with the aid of a microscope, attached to a glass fiber, and immediately placed in the low-temperature N_2 stream of the diffractometer.[21] The intensity data sets for all compounds were collected by using a Siemens SMART system, complete with three-circle goniometer and CCD detector operating at −54 °C. Data for compounds **1–4** were collected at 93, 92, 91, and 94 K, respectively, by using a custom build low-temperature device from Professor H. Hope (UC Davis). In all cases graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ 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 angle, and each exposure covering 0.3° in θ. 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 for all compounds by utilizing the program SADABS.[22] The crystal structures of all compounds were solved by Direct Methods as included in the SHELXTL-Plus program package.[23] Missing atoms were located in subsequent difference Fourier maps and included in the refinement. The structures of all compounds were refined by full-matrix least-squares refinement on F^2 (SHELX-93). Hydrogen atoms were placed geometrically and refined using a riding model, including free rotation about C–C bonds for methyl groups 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 crystallographic programs used for structure refinement and solution 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 disordered positions were refined anisotropically. Complex **3** [Mg(5-CF$_3$-pyS)$_2$(thf)$_2$] contains a particularly disordered THF unit situated in holes in the crystalline network. The THF molecules were removed from the structure so that a better refinement could be obtained using the Squeeze program, as implemented in Platon.[24] The electron density and hole size agree well with the solvent being THF. Crystallographic data for compounds **1–4** are given in Table 2.

CCDC 190681–1900684 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.hmtl (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax; (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Table 2. Crystallographic data for compounds **1–4**.

	1	**2**	**3**	**4**
formula	$C_{20}H_{28}N_2O_{2.5}S_2Mg$	$C_{20}H_{22}F_6N_2O_2S_2Mg$	$C_{20}H_{22}F_6N_2O_2S_2Mg$	$C_{27}H_{46}N_2O_{2.5}S_2Si_2Mg$
M_r	424.87	524.83	524.82	583.27
space group	$C2/c$	$P2_1/c$	$C2/c$	$P2_1/c$
a [Å]	18.0422(8)	11.5166(3)	11.8701(10)	7.7671(6)
b [Å]	8.5300(4)	15.9296(4)	14.3283(12)	15.6038(12)
c [Å]	28.1874(13)	12.6799(3)	16.3295(13)	26.696(2)
β [°]	99.138(1)	98.859(2)	96.131(2)	95.287(1)
V [Å^3]	4283.0(3)	2298.44(11)	2761.4(4)	3221.7(4)
Z	8	4	4	4
μ [mm^{-1}]	0.298	0.328	0.273	0.287
$R1/wR2$ (all data)[a]	0.0476/0.0894	0.0785/0.1185	0.0489/0.0821	0.0870/0.1397
$R1/wR2$ ($>2\sigma$)	0.0364/0.0847	0.0490/0.1074	0.0335/0.0791	0.0544/0.1244

a] $R1 = \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \sqrt{\Sigma w\{(F_o)^2 - (F_c)^2\}^2/\Sigma w\{(F_o)^2\}^2}$.

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