

Synthesis and Structure of Unassociated Mono-, Di-, and Trithiolate Derivatives of Aluminum and Gallium: Investigation of Al–S and Ga–S π -Bonding

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The synthesis and characterization of several sterically crowded aluminum and gallium thiolates are described. The major reason for these studies was the investigation of the possible occurrence of π -bonding in Al–S and Ga–S bonds and the determination of the steric requirements for the isolation of monomeric heavier main group 3 thiolates in the solid state. The compounds examined were $\text{RAl}(\text{SMes}^*)_2$ ($\text{R} = n\text{-Bu}$, **1**; $t\text{-Bu}$, **2**), $\text{Mes}^*_2\text{GaSR}$ ($\text{Mes}^* = 2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2$, $\text{R} = \text{Me}$, **3**; Ph , **4**), $n\text{-BuGa}(\text{SMes}^*)_2$, (**5**) ($t\text{-Bu}_2\text{AlSTrip}$)₂ (**6**) ($\text{Trip} = 2,4,6\text{-}i\text{-Pr}_3\text{C}_6\text{H}_2$), $(\text{THF})\text{Al}(\text{STrip})_3$ (**7**). They were characterized by X-ray crystallography (**1**–**3**, **5**–**7**) and by NMR and IR spectroscopy. The data indicate that the M–S, p–p, π -bonding is weak and has an upper limit of 8–9 kcal mol⁻¹. Restricted rotation around an M–S bond was detected only in the cases of $\text{Mes}^*_2\text{GaSMe}$ (**3**) and $\text{Mes}^*_2\text{-GaSPh}$ (**4**). Crystal data at 130 K with Mo K α ($\lambda = 0.71069 \text{ \AA}$) (**2**, **5**–**7**) or Cu K α ($\lambda = 1.54178 \text{ \AA}$) (**1**, **3**) radiation; **1**, $n\text{-BuAl}(\text{SMes}^*)_2$, $\text{C}_{40}\text{H}_{67}\text{AlS}_2$, $a = 18.563(5) \text{ \AA}$, $b = 27.171(11) \text{ \AA}$, $c = 32.089(4) \text{ \AA}$, orthorhombic, $Z = 16$ (two independent molecules), space group $Pbca$, $R = 0.087$ for 6746 ($I > 2\sigma(I)$) data; **2**, $t\text{-BuAl}(\text{SMes}^*)_2$, $\text{C}_{40}\text{H}_{67}\text{AlS}_2$, $a = 17.375(9) \text{ \AA}$, $b = 27.982(10) \text{ \AA}$, $c = 17.868(8) \text{ \AA}$, $\beta = 112.29(2)^\circ$, $Z = 8$ (two independent molecules), monoclinic, space group $P2_1/c$, $R = 0.082$ for 8425 ($I > 2\sigma(I)$) reflections; **3**, $\text{Mes}^*_2\text{GaSMe}$, $\text{C}_{37}\text{H}_{61}\text{-GaS}$, $a = 33.654(8) \text{ \AA}$, $b = 10.433(4) \text{ \AA}$, $c = 20.258(8) \text{ \AA}$, $Z = 8$, orthorhombic, space group $Pbcn$, $R = 0.066$ for 3164 ($I > 2\sigma(I)$) reflections; **5**, $n\text{-BuGa}(\text{SMes}^*)_2$, $\text{C}_{40}\text{H}_{67}\text{GaS}_2$, $a = 18.521(8) \text{ \AA}$, $b = 27.342(10) \text{ \AA}$, $c = 32.046(12) \text{ \AA}$, orthorhombic, $Z = 16$ (two independent molecules), space group $Pbca$, $R = 0.144$ for 3297 ($I > 2\sigma(I)$) reflections; **6**, ($t\text{-Bu}_2\text{AlSTrip}$)₂, $\text{C}_{46}\text{H}_{82}\text{Al}_2\text{S}_2$, $a = 20.820(8) \text{ \AA}$, $b = 14.598(6) \text{ \AA}$, $c = 16.118(4) \text{ \AA}$, $Z = 4$, orthorhombic, space group $Pna2_1$, $R = 0.062$ for 2469 ($I > 2.5\sigma(I)$) data; **7**, $(\text{THF})\text{Al}(\text{STrip})_3 \cdot 0.5\text{C}_6\text{H}_{14}$, $\text{C}_{52}\text{H}_{84}\text{-AlO}_3$, $a = 15.589(6) \text{ \AA}$, $b = 13.622(5) \text{ \AA}$, $c = 26.308(12) \text{ \AA}$, $\beta = 99.88(2)^\circ$, $Z = 4$, monoclinic, space group $P2_1/c$, $R = 0.075$ for 5697 ($I > 3\sigma(I)$) data.

Introduction

Compounds of formula $\text{R}_n\text{M}(\text{ER}')_{3-n}$ ($\text{M} = \text{Al-Tl}$, $\text{E} = \text{S-Te}$, R and $\text{R}' = \text{alkyl or aryl group}$, $n = 0, 1, \text{ or } 2$) have been known and studied for many years.¹ Yet, it is only within the past decade or so that a significant amount of detailed information on the structure and reactivity of such species has become available. The data show that the compounds have a very strong tendency to associate through bridging of the metals by the chalcogenide groups. Most typically, dimeric or trimeric aggregates are formed. Monomeric derivatives are very rare, and at present, the only such compounds to have been described in detail are the trichalcogenolates $\text{M}(\text{SMes}^*)_3$ ($\text{M} = \text{Al},^2 \text{ Ga},^2 \text{ or In}^3$), $\text{M}(\text{SeMes}^*)_3$ ($\text{M} = \text{Ga}^4 \text{ or In}^3$), the tellurolate $\{(\text{Me}_3\text{-Si})_2\text{CH}\}_2\text{GaTeSi}(\text{SiMe}_3)_3$,⁵ and the chalcogenide-bridged species $\text{E}[\text{Al}\{\text{CH}(\text{SiMe}_3)_2\}_2]_2$ ($\text{E} = \text{S}^6 \text{ or Te}^7$). These unassociated species are of interest since the metal is coordinatively unsaturated (three-coordinate). Thus, the metal bears an empty p-orbital which may interact with one or more of the electron lone pairs of the chalcogen to form a π -bond. Recent work on related Al–O species $t\text{-Bu}_{3-n}\text{Al}(\text{OR})_n$ ($\text{R} = 2,6\text{-}t\text{-Bu}_2\text{-4-MeC}_6\text{H}_2$, $n =$

$1,^{8a} 2,^{8b}$ or 3^{8c}) has shown that the Al–O bond length decreases when the number of aryloxy groups increases (vide infra). This is contrary to what is expected if conventional p–p, Al–O π -bonding were significant. In this paper the syntheses of a series of related, low-coordinate, aluminum and gallium thiolate compounds are described. These compounds were examined both structurally and spectroscopically, and the data are interpreted in light of the possible existence of π -interactions in the less polar and more evenly size-matched M–S ($\text{M} = \text{Al}$ or Ga) atom pairs.

Experimental Section

General Procedures. All experiments were performed either by the use of modified Schlenk techniques or in a Vacuum Atmospheres HE43-2 drybox under a nitrogen atmosphere. Solvents were freshly distilled from a Na/K alloy and degassed twice prior to use. ¹H NMR spectra were recorded in C₆D₆ or C₇D₈ solutions by using a General Electric QE-300 spectrometer. Infrared spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer PE-1470 spectrometer.

Starting Materials. GaCl₃ (Strem), NaSMe, and $n\text{-BuLi}$ (1.6 M in hexanes) (Aldrich) were obtained commercially and used as received without further purification. AlBr₃ (Alfa) was purified by vacuum sublimation. HSMes*,⁹ TripSH,¹⁰ $t\text{-Bu}_2\text{AlH}$,¹¹ $\text{Ga}(n\text{-Bu})_3$,¹² and Mes^*_2 -

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GaCl¹³ were prepared according to literature methods and spectroscopically characterized.

***n*-BuAl(SMes*)₂ (1).** HSMes* (1.11 g, 4 mmol) was dissolved in toluene (40 mL) with cooling in an ice bath, and *n*-BuLi (2.75 mL of a 1.6 M solution in hexanes, 10% excess) was added slowly by syringe. The mixture was allowed to warm to room temperature and stirred for a further 2 h. This solution was added dropwise to a solution of AlBr₃ (0.48 g, 2 mmol) in toluene (20 mL), and the mixture was stirred for 18 h. Filtration, followed by removal of the toluene under reduced pressure to afford a ca. 20 mL solution, gave upon cooling in a -20 °C freezer, colorless plates of the product in 29% (0.37 g) yield. Mp: 141–143 °C (gas evolved at 148 °C). ¹H NMR (C₆D₆): δ 7.46 (s, *m*-H, 4H), 1.72 (s, *o*-CH₃, 36H), 1.27 (s, *p*-CH₃, 18H), 0.82 (m, β- or γ-CH₂, 2H), 0.56 (t, δ-CH₃, 3H), ³J_{HH} = 7.2 Hz, 0.42 (m, β- or γ-CH₂, 2H), -0.42 (m, α-CH₂, 2H). ¹³C{¹H} NMR: δ 153.6 (*o*-C), 148.3 (*p*-C), 142.0 (ipso-C), 122.6 (*m*-C), 38.2 (*o*-C(CH₃)₃), 34.9 (*p*-C(CH₃)₃), 32.3 (*o*-CH₃), 31.5 (*p*-CH₃), 28.0, 25.3 (β- and γ-CH₂), 13.2 (δ-CH₃), 10.1 (broad s, α-CH₂).

***t*-BuAl(SMes*)₂ (2).** *t*-Bu₂AlH (1.1 g, 7.72 mmol), dissolved in hexane (20 mL), was treated dropwise with a solution of HSMes* (2.15 g, 7.72 mmol) in hexane (30 mL). The reaction commenced immediately, and gas evolution was readily apparent. Stirring was continued for 2 h, after which the solution was filtered. The colorless filtrate was concentrated to ca. 15 mL. Storage at ca. -40 °C for 12 h gave the product as colorless blocks in 41% yield (2.0 g). Mp: 139–141 °C. ¹H NMR: δ 7.46 (s, 4H, *m*-H), 1.59 (s, 36H, *o*-*t*-Bu), 1.31 (s, 18H, *p*-*t*-Bu), 1.27 (s, 9H, *t*-Bu).

Mes*₂GaSMes (3). With cooling in an ice bath and rapid stirring, a solution of Mes*₂GaCl (0.89 g, 1.49 mmol) in THF (10 mL) was added to a slurry of 0.11 g (1.5 mmol) of NaSMes in THF (20 mL). The mixture was kept at 0 °C for 0.5 h, allowed to come to room temperature, and stirred for a further 16 h. The solvent was removed under reduced pressure, and the residue was extracted with hexane (60 mL). After filtration, the colorless solution was concentrated to ca. 4 mL and stored at -20 °C for 3 days to afford the product (0.4 g) as colorless crystals suitable for X-ray crystallographic studies. Further concentration of the supernatant liquid to ca. 1 mL afforded a further crop (0.35 g) of crystals of 3. Yield: 0.75 g (1.24 mmol, 83%). Mp: 153–156 °C. ¹H NMR (C₇D₈): δ 7.45 (s, 4H, *m*-H), 1.73 (s, 3H, SCH₃), 1.48 (s, 36H, *o*-*t*-Bu), 1.30 (s, 18H, *p*-*t*-Bu). ¹³C{¹H} NMR (C₇D₈): δ 157.9 (*o*-C), 150.2 (*p*-C), 136.1 (ipso-C), 122.7 (*m*-C), 38.8 (*o*-C(CH₃)₃), 34.6 (*p*-C(CH₃)₃), 33.4 (*o*-C(CH₃)₃), 31.3 (*p*-C(CH₃)₃), 12.2 (SCH₃). IR: 343 cm⁻¹ (ν_{Ga-S}).

Mes*₂GaSPH (4). A solution of Mes*₂GaCl (1.20 g, 2.0 mmol) in hexane (50 mL) was added to a slurry of LiSPH in Et₂O (20 mL) with rapid stirring (generated in situ by treatment of PhSH (0.21 mL, 2.05 mmol, in ether with 1.3 mL (2.1 mmol) of the *n*-BuLi solution). Stirring was continued for 20 h at room temperature and for a further 3 h at reflux temperature. After filtration, the colorless solution was concentrated to ca. 5 mL and stored at -20 °C in order to obtain crystals. No crystallization was effected from small volumes of this solvent or the pure solvents, toluene, Et₂O, or pentane. Removal of all the volatile material under reduced pressure, however, afforded a viscous oil which solidified upon standing for 2 days at room temperature. Mp: 134–135 °C. ¹H NMR (C₆D₆): δ 7.46 (s, 4H, *m*-H), 7.04 (m, 2H, SPh), 6.74 ("d", 3H, Δν = 1.8 Hz, SPh), 6.72 ("d", Δν = 1.8 Hz, SPh), 1.49 (s, 36H, *o*-*t*-Bu), 1.29 (s, 18H, *p*-*t*-Bu). ¹³C{¹H} NMR (C₆D₆): δ 157.8 (*o*-C), 150.5 (*p*-C), 137.2 (ipso-C), 137.4 (ipso-C, SPh), 134.9 (*o*-C, SPh), 128.1 (*m*-C, SPh), 125.4 (*p*-C, SPh), 39.0 (*o*-C(CH₃)₃), 34.6 (*p*-C(CH₃)₃), 33.4 (*o*-C(CH₃)₃), 31.4 (*p*-C(CH₃)₃). IR: 333 cm⁻¹ (ν_{Ga-S}).

***n*-BuGa(SMes*)₂ (5).** A solution of HMes* (1.39 g, 5 mmol) in *n*-hexane (30 mL) was added slowly to a solution of Ga(*n*-Bu)₃ (0.60 g, 2.5 mmol) in *n*-hexane (20 mL). The reaction mixture was stirred for 60 h to afford a clear, pale-yellow solution. The solution was concentrated to ca. 10 mL under reduced pressure and cooled in a -20 °C freezer to afford the product 5 as colorless crystals. Yield: 1.19 g, 69%. Mp: 200–210 °C. ¹H NMR (C₆D₆): δ 7.46 (s, 4H, *m*-H), 1.69 (s, 36H, *o*-*t*-Bu), 1.27 (s, 18H, *p*-*t*-Bu), 0.79 (m, β- or γ-CH₂, 2H),

0.54 (t, δ-CH₃, 3H), ³J_{HH} = 7.2 Hz, 0.49 (m, β- or γ-CH₂, 2H), 0.14 (m, α-CH₂, 2H). ¹³C{¹H} NMR (C₆D₆): δ 153.8 (*o*-C), 148.5 (*p*-C), 142.0 (ipso-C), 122.4 (*m*-C), 38.3 (*o*-C(CH₃)₃), 35.7 (*p*-C(CH₃)₃), 32.4 (*o*-CH₃), 31.5 (*p*-CH₃), 27.2 (β-CH₂), 26.0 (γ-CH₂), 18.5 (δ-CH₃), 13.1 (α-CH₂).

(*t*-Bu)₂AlStrip)₂ (6). *t*-Bu₂AlH (0.43 g, 3 mmol) was dissolved in pentane (10 mL), and TripSH (0.71 g, 2 mmol) in pentane (10 mL) was added dropwise via a double-tipped needle. The reaction commenced immediately, and vigorous gas evolution was observed. The clear, colorless solution was stirred for 2 h, after which it was concentrated to ca. 5 mL under reduced pressure. Storage for 12 h in a -40 °C freezer afforded the product as colorless plates. Yield: 0.975 g (86.3%). Mp: 156–158 °C. ¹H NMR (C₆D₆): δ 7.11 (s, 4H, *m*-H), 4.10 (sept, 4H, *o*-CH(CH₃)₂), 2.70 (sept, 2H, *p*-CH(CH₃)₂), 1.43 (d, 24H, *o*-CH(CH₃)₂), 1.19 (d, 12H, *p*-CH(CH₃)₂). IR: ν_{Al-S} 418, 398, 362 cm⁻¹.

(THF)Al(STrip)₃ (7). With cooling in an ice bath, TripSH (1.34 g, 5.67 mmol) was dissolved in Et₂O (30 mL), and the solution was treated dropwise with *n*-BuLi (3.7 mL of a 1.6 M solution in hexane). This solution was stirred at room temperature for 2 h, and AlCl₃·THF (0.56 g, 2.84 mmol) dissolved in Et₂O (40 mL) was added dropwise. The solution became cloudy, and stirring was continued for a further 18 h. The solution was then filtered, and the clear filtrate was concentrated to ca. 20 mL. Cooling in a -20 °C freezer afforded the product as colorless crystals. Yield: 0.983 g (43%). Mp: 132–134 °C. ¹H NMR (C₆D₆): δ 7.10 (s, 6H, *m*-H), 4.00 (sept, 6H, *o*-CH(CH₃)₂), ³J_{HH} = 6.6 Hz, 3.68 (s, broad, 4H, OCH₂(THF)), 2.81 (sept, 3H, *p*-CH(CH₃)₂), ³J_{HH} = 6.9 Hz, 1.34 (d, 36H, *o*-CH₃), 1.25 (d, 18H, *p*-CH₃), 0.84 (s, broad, 4H, CH₂(THF)). ¹³C NMR (C₆D₆): δ 152.2 (*o*-C), 146.7 (*p*-C), 128.7 (ipso-C), 121.2 (*m*-C), 73.9 (OCH₂(THF)), 34.6 (*p*-CH(CH₃)₂), 33.0 (*o*-CH(CH₃)₂), 24.4 (*p*-CH₃), 23.9 (*o*-CH₃).

X-ray Data Collection and Solution and Refinement of Structures. The crystals of 1–3 and 5–7 were transferred from the Schlenk tube onto a Petri dish and immediately covered with a layer of hydrocarbon oil. Single crystals were selected, mounted on a glass fiber, and immediately placed in the low-temperature N₂ stream as described in ref 14. The X-ray data for compounds 2 and 5–7 were collected on a Siemens R3m/V diffractometer; those for 1 and 3 were collected with a Syntex P2₁ diffractometer. Calculations were performed on a Micro Vax 3200 using the SHELXTL PLUS program system for 3, 6, and 7, SHELXL-93 for 1, and SHELXTL for 2 and 5 on a 486 IBM computer. The atomic form factors including anomalous scattering factors were taken from the usual sources.^{15a} All non-hydrogen atoms were refined anisotropically except in the case of 5, where the Ga and S atoms only were so refined. An absorption correction was applied using the method described in ref 15b,c. The structures of 1, 2, 5, and 7 were also subject to minor disorder problems. In 1 and 5 the *n*-butyl group and the para *tert*-butyl C(70)–C(72) of the second molecule in the asymmetric unit were refined isotropically with occupancies of 49% (1), 60% (5), 48.3% (1), and 40% (5), respectively. The structure of 2 features disorder of the para *tert*-butyl group C(34)–C(36), which was modeled with 64.3% occupancy. Finally, the hexane solvent molecule in 7 was refined isotropically without hydrogen atoms on two split positions with 25% occupancy each. In the case of 5 several crystals grown from different solvents were tried, all of which diffracted poorly despite their adequate size and their being well-formed. The crystal used gave only 3297 reflections with $I > 2\sigma(I)$ out of 12 986, but the structure, which is isomorphous with 1, could be successfully refined up to $R_1 = 0.144$. Table 1 summarizes the crystal data and refinement parameters for the data collections. Important atom coordinates, bond distances, and bond angles are presented in Tables 2 and 3.

Results

Syntheses. Since both aluminum and gallium halides form strong adducts with Lewis bases, the use of donor solvents was

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Table 1. Crystallographic Data for 1–3 and 5–7

	<i>n</i> -BuAl(SMes*) ₂ (1)	<i>t</i> -BuAl(SMes*) ₂ (2)	Mes* ₂ GaSMes (3)	<i>n</i> -BuGa(SMes*) ₂ (5)	(<i>t</i> -Bu ₂ AlSTrip) ₂ (6)	(THF)Al(STrip) ₃ ·0.5C ₆ H ₁₄ (7)
formula	C ₄₀ H ₆₇ AlS ₂	C ₄₀ H ₆₇ AlS ₂	C ₃₇ H ₆₁ GaS	C ₄₀ H ₆₇ GaS ₂	C ₄₆ H ₈₂ Al ₂ S ₂	C ₅₂ H ₈₄ AlOS ₃
fw	639.04	639.04	607.6	681.8	753.2	848.4
cryst syst	orthorhombic	monoclinic	orthorhombic	orthorhombic	orthorhombic	monoclinic
color, habit	colorless plates	colorless blocks	colorless blocks	colorless plates	colorless plates	colorless parallelepipeds
space group	<i>Pbca</i>	<i>P2₁/c</i>	<i>Pbcn</i>	<i>Pbca</i>	<i>Pna2₁</i>	<i>P2₁/c</i>
<i>a</i> , Å	18.563(5)	17.375(9)	33.654(8)	18.521(8)	20.820(8)	15.589(6)
<i>b</i> , Å	27.171(11)	27.982(10)	10.433(4)	27.342(10)	14.598(6)	13.622(5)
<i>c</i> , Å	32.089(4)	17.868(8)	20.258(8)	32.046(12)	16.118(4)	26.308(12)
α, deg						
β, deg		122.29(2)				99.88(2)
γ, deg						
<i>V</i> , Å ³	16185(8)	8038(6)	7113(4)	16228(11)	4899(3)	5504(4)
<i>Z</i>	16	8	8	16	4	4
<i>d</i> (calc), g cm ⁻³	1.049	1.056	1.135	1.116	1.021	1.024
linear abs coeff, mm ⁻¹	1.562	0.179	1.746	0.805	0.172	0.182
2θ range, deg	0–114	0–55	0–115	0–48	0–52	0–55
no. of obsd reflns	6746 (<i>I</i> > 2σ(<i>I</i>))	8425 (<i>I</i> > 2σ(<i>I</i>))	3164 (<i>I</i> > 2σ(<i>I</i>))	3297 (<i>I</i> > 2σ(<i>I</i>))	2469 (<i>I</i> > 2.5σ(<i>I</i>))	5697 (<i>I</i> > 3σ(<i>I</i>))
no. of variables	812	767	352	402	450	535
<i>R</i> (<i>F</i>); <i>R</i> _w (<i>F</i>)	0.087	0.082	0.066; 0.062	0.144	0.062; 0.076	0.075; 0.089

Table 2. Atom Coordinates (×10⁴) for Important Atoms in 1–3 and 5–7

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
Compound 1							
Al(1)	3212(1)	1495(1)	133(1)	Al(2)	5706(1)	2489(1)	2570(1)
S(1)	3912(1)	865(1)	-5(1)	S(3)	6447(1)	1875(1)	2688(1)
S(2)	3861(1)	2154(1)	249(1)	S(4)	6337(1)	3167(1)	2546(1)
C(1)	3223(3)	398(2)	56(2)	C(41)	5767(3)	1397(1)	2671(2)
C(19)	3147(3)	2605(2)	193(2)	C(59)	5612(3)	3603(2)	2470(2)
C(37)	2167(3)	1467(2)	181(2)	C(77)	4687(7)	2532(5)	2453(4)
C(38)	1685(4)	1645(4)	-119(3)	C(78)	4195(7)	2186(5)	2722(4)
C(39)	870(4)	1587(4)	-31(2)	C(79)	3410(8)	2295(6)	2666(5)
C(40)	428(5)	1854(3)	-319(2)	C(80)	3160(9)	2790(5)	2854(5)
Compound 2							
Al(1)	4743(1)	7869(1)	2697(1)	Al(2)	163(1)	906(1)	2414(1)
S(1)	3890(1)	7288(1)	2675(1)	S(3)	572(1)	259(1)	1974(1)
S(2)	4167(1)	8494(1)	3021(1)	S(4)	1030(1)	1448(1)	2309(1)
C(1)	5751(3)	7831(1)	2427(3)	C(41)	-778(3)	991(2)	2778(3)
C(5)	4515(3)	6771(1)	2680(3)	C(45)	176(2)	-214(1)	2413(2)
C(23)	4621(2)	8989(1)	2680(2)	C(63)	465(2)	1998(1)	2261(2)
Compound 3							
Ga(1)	4036(1)	2090(1)	4994(1)	C(19)	3763(2)	1219(6)	5738(3)
S(1)	4193(1)	570(2)	4236(1)	C(37)	4127(2)	-920(7)	4692(4)
C(1)	4058(2)	3907(6)	4679(3)				
Compound 5							
Ga(1)	1824(1)	1485(1)	123(1)	Ga(2)	9303(1)	2439(1)	2580(1)
S(1)	1180(3)	2158(2)	206(2)	S(3)	8554(3)	1822(2)	2688(2)
S(2)	1095(3)	853(2)	18(2)	S(4)	8675(3)	3124(2)	2578(2)
C(1)	1890(10)	2597(7)	176(6)	C(41)	9237(12)	1339(7)	2677(6)
C(19)	1793(11)	386(7)	63(6)	C(59)	9402(11)	3554(7)	2488(7)
C(37)	2885(10)	1424(8)	174(7)	C(77)	10372(21)	2282(18)	2588(20)
C(38)	3339(9)	1694(9)	-110(7)	C(78)	10826(16)	2665(13)	2406(13)
C(39)	4160(9)	1585(8)	-49(7)	C(79)	11646(15)	2545(17)	2421(10)
C(40)	4628(11)	1907(9)	-326(7)	C(80)	11947(23)	2443(20)	2847(12)
Compound 6							
Al(1)	977(1)	-284(2)	4800(2)	C(5)	1172(5)	-927(7)	3751(6)
Al(2)	2311(1)	783(2)	5977(3)	C(9)	3066(5)	1306(7)	5378(13)
S(1)	1452(1)	1158(1)	5062(2)	C(13)	2274(8)	814(9)	7216(9)
S(2)	1792(1)	-684(1)	5759(2)	C(17)	1100(4)	2263(5)	4796(7)
C(1)	79(5)	-222(7)	5227(8)	C(32)	2077(4)	-1846(5)	5732(7)
Compound 7							
Al(1)	6456(1)	3138(1)	812(1)	O(1)	5659(2)	3909(3)	1082(1)
S(1)	5961(1)	1602(1)	819(1)	C(1)	4888(3)	1684(4)	972(2)
S(2)	6438(1)	3886(1)	55(1)	C(16)	7403(3)	3342(4)	-117(2)
S(3)	7763(1)	3349(1)	1285(1)	C(31)	7843(3)	2452(4)	1786(2)

generally avoided. Nonetheless, prior work has shown that the Mes* group is effective at stabilizing three-coordination at Al and Ga in donor solvents so that both 3 and 4 could be prepared by salt elimination in THF solution without the risk of adduct formation.^{13,16} The synthesis of the adduct 7 was undertaken when attempts to crystallize and purify Al(STrip)₃ in hydro-

carbon solvent proved unsuccessful. It was hoped that this compound could be isolated through desolvation of 7 by heating (100 °C) under high vacuum for several hours. However, ¹H

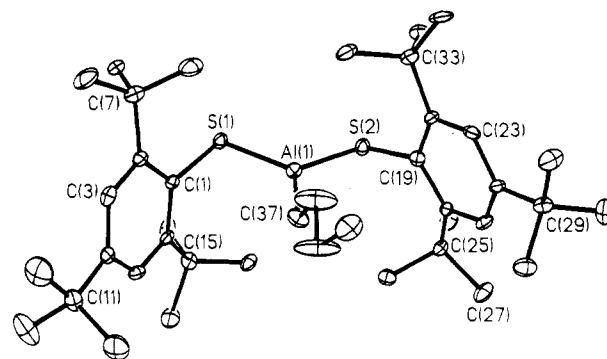
(16) Petrie, M. A.; Power, P. P.; Dias, H. V. R.; Ruhlandt-Senge, K.; Waggoner, K.; Wehmschulte, R. *Organometallics* 1993, 12, 1086.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compounds 1–3 and 5–7

Compound 1			
Al(1)–S(1)	2.194(2)	S(1)–Al(1)–S(2)	110.23(9)
Al(1)–S(2)	2.191(2)	S(1)–Al(1)–C(37)	125.2(2)
Al(1)–C(37)	1.947(6)	S(2)–Al(1)–C(37)	124.5(2)
Al(2)–S(3)	2.195(2)	S(3)–Al(2)–S(4)	108.14(10)
Al(2)–S(4)	2.184(2)	S(3)–Al(2)–C(77)	133.9(4)
Al(2)–C(77)	1.932(13)	S(4)–Al(2)–C(77)	117.8(4)
S(1)–C(1)	1.812(5)	Al(1)–S(1)–C(1)	96.1(2)
S(2)–C(19)	1.814(6)	Al(1)–S(2)–C(19)	97.7(2)
S(3)–C(41)	1.810(6)	Al(2)–S(3)–C(41)	95.9(2)
S(4)–C(59)	1.810(6)	Al(2)–S(4)–C(59)	99.2(2)
Compound 2			
Al(1)–S(1)	2.190(2)	S(1)–Al(1)–S(2)	102.92(7)
Al(1)–S(2)	2.197(2)	S(1)–Al(1)–C(1)	127.39(14)
Al(1)–C(1)	1.988(4)	S(2)–Al(1)–C(1)	129.61(13)
Al(2)–S(3)	2.197(2)	S(3)–Al(2)–S(4)	102.32(7)
Al(2)–S(4)	2.196(2)	S(3)–Al(2)–C(41)	129.28(14)
Al(2)–C(41)	1.990(4)	S(4)–Al(2)–C(41)	128.36(14)
S(1)–C(5)	1.807(4)	Al(1)–S(1)–C(5)	101.19(14)
S(2)–C(23)	1.810(4)	Al(1)–S(2)–C(23)	102.72(13)
S(3)–C(45)	1.803(4)	Al(2)–S(3)–C(45)	102.69(13)
S(4)–C(63)	1.809(4)	Al(2)–S(4)–C(63)	102.38(13)
Compound 3			
Ga(1)–S(1)	2.271(2)	C(1)–Ga(1)–C(19)	133.9(3)
Ga(1)–C(1)	2.001(6)	C(1)–Ga(1)–S(1)	115.9(2)
Ga(1)–C(19)	1.984(7)	C(19)–Ga(1)–S(1)	107.5(2)
S(1)–C(37)	1.823(8)	Ga(1)–S(1)–C(37)	102.9(3)
Compound 5			
Ga(1)–S(1)	2.208(9)	S(1)–Ga(1)–S(2)	109.7(3)
Ga(1)–S(2)	2.220(9)	S(1)–Ga(1)–C(37)	126.7(11)
Ga(1)–C(37)	1.98(3)	S(2)–Ga(1)–C(37)	123.4(10)
Ga(2)–S(3)	2.211(6)	S(3)–Ga(2)–S(4)	108.5(2)
Ga(2)–S(4)	2.204(6)	S(3)–Ga(2)–C(77)	116.7(13)
Ga(2)–C(77)	2.03(4)	S(4)–Ga(2)–C(77)	134.0(14)
S–C (av.)	1.81(2)	Ga–S–C	97.6(1.0)
Compound 6			
Al(1)–S(1)	2.365(3)	S(1)–Al(1)–S(2)	78.7(1)
Al(1)–S(2)	2.368(4)	S(1)–Al(2)–S(2)	77.2(1)
Al(1)–C(1)	1.995(10)	Al(1)–S(1)–Al(2)	102.7(1)
Al(1)–C(5)	1.976(11)	Al(1)–S(2)–Al(2)	101.3(1)
Al(2)–S(1)	2.381(4)	C(1)–Al(1)–C(5)	120.6(5)
Al(2)–S(2)	2.424(4)	C(9)–Al(2)–C(13)	120.3(7)
Al(2)–C(9)	1.997(14)	Al(1)–S(1)–C(17)	125.3(3)
Al(2)–C(13)	2.000(15)	Al(2)–S(1)–C(17)	130.7(3)
		Al(1)–S(2)–C(32)	117.0(3)
		Al(2)–S(2)–C(32)	133.6(3)
Compound 7			
Al(1)–S(1)	2.232(2)	S(1)–Al(1)–S(2)	119.0(1)
Al(1)–S(2)	2.231(2)	S(1)–Al(1)–S(3)	113.7(1)
Al(1)–S(3)	2.217(2)	S(2)–Al(1)–S(3)	108.2(1)
Al(1)–O(1)	1.859(4)	S(1)–Al(1)–O(1)	105.8(1)
S(1)–C(1)	1.790(6)	S(2)–Al(1)–O(1)	100.1(1)
S(2)–C(16)	1.803(5)	S(3)–Al(1)–O(1)	108.8(1)
S(3)–C(31)	1.786(6)	Al(1)–S(1)–C(1)	106.3(2)
		Al(1)–S(2)–C(16)	98.8(2)
		Al(1)–S(3)–C(31)	105.5(2)

NMR spectroscopic data revealed no diminution in the intensity of the THF signals.

Compounds **1** and **5** were initially discovered fortuitously during attempts to synthesize $\text{XM}(\text{SMes}^*)_2$ ($\text{X} = \text{Cl}$ or Br ; $\text{M} = \text{Al}$ or Ga). These attempted syntheses involved treatment of MX_3 with 2 equiv of LiSMes^* . This did not result in the isolation of the desired products. Instead compounds **1** and **5** were obtained in a low yield, presumably as a result of the presence of unreacted or excess $n\text{-BuLi}$ in the LiSMes^* slurry used for their syntheses. It is perhaps, worth noting that, in order to obtain good yields of $\text{M}(\text{SMes}^*)_3$, it is necessary to wash the precipitated LiSMes^* solid with pentane in order to remove any $n\text{-BuLi}$. A more readily reproducible synthesis of **5** involves the treatment of the known compound $\text{Ga}(n\text{-Bu})_3$ ¹² with 2 equiv of HSMes^* . The synthesis of the related species

**Figure 1.** Thermal ellipsoid (30%) plot of one of the asymmetric unit molecules of **1**. Hydrogens are omitted for clarity.

$t\text{-BuAl}(\text{SMes}^*)_2$ (**2**) was also inadvertent. It was desired to synthesize an unassociated aluminum monothiolate $t\text{-Bu}_2\text{-AlSMes}^*$ by treatment of $t\text{-Bu}_2\text{AlH}$ with 1 equiv of HSMes^* . The only product that could be crystallized from the reaction mixture was $t\text{-BuAl}(\text{SMes}^*)_2$ (**2**) as well as some $t\text{-Bu}_2\text{AlH}$. The presence of **2** may arise from the disproportionation of $t\text{-Bu}_2\text{AlSMes}^*$. Alternatively, it is possible that $t\text{-Bu}_2\text{AlSMes}^*$ can react with HSMes^* to give **2**. The possibility of disproportionation receives support from the attempted preparation of $\text{Br}_2\text{AlSMes}^*$ (via the reaction of 1 equiv of LiSMes^* with AlBr_3) which resulted in the isolation of $\text{Al}(\text{SMes}^*)_3$ rather than the expected monosubstituted product. It is notable, however, that the dimeric compound $(t\text{-Bu}_2\text{AlSTrip})_2$ (**6**) is quite stable and displays no tendency to disproportionate at temperatures as high as its melting point in excess of 150 °C.

Structural Descriptions. $n\text{-BuAl}(\text{SMes}^*)_2$ (**1**). The crystallographic data for **1** show that there are two crystallographically independent $n\text{-BuAl}(\text{SMes}^*)_2$ molecules in the asymmetric unit. These are well-separated and feature aluminum bound in a trigonal planar fashion by two -SMes^* and an $n\text{-Bu}$ group as shown in Figure 1. The -SMes^* groups have a *Z*-conformation ($\text{S}-\text{Al}-\text{S} = 109.2(1.0)^\circ$) with respect to the $n\text{-Bu}$ group with averaged $\text{Al}-\text{S}$ and $\text{Al}-\text{C}$ distances of 2.191(4) and 1.950(14) Å. The $\text{Al}-\text{S}-\text{C}$ angles are in the range 95.9(2)–99.2(2)°. Minor differences between the two molecules in the asymmetric unit relate to greater differences in the $\text{C}-\text{Al}-\text{S}$ angles (0.7° in the $\text{Al}(1)$ molecule vs 16.1° at $\text{Al}(2)$) and lower $\text{Al}-\text{S}$ bond torsion angles in the $\text{Al}(2)$ molecule (2.5 and 3.3° for $\text{Al}(2)$ vs 12.6 and 17.5° for $\text{Al}(1)$).

$t\text{-BuAl}(\text{SMes}^*)_2$ (**2**). The structure of **2** (Figure 2) is very similar to that of **1**. The asymmetric unit also involves two crystallographically independent molecules. The aluminum atoms have three-coordinate planar geometry with average $\text{Al}-\text{S}$ distances of 2.194(2) and 2.197(2) Å and $\text{Al}-\text{C}$ bond lengths of 1.988(4) and 1.990(4) Å. The $\text{S}-\text{Al}-\text{S}$ angles, 102.9(1) and 102.3(1)°, are significantly narrower than the $\text{S}-\text{Al}-\text{C}$ angles, which average 128.5 and 128.8°. The Mes^*S groups are in the *Z*-conformation with respect to the $t\text{-Bu}$ group. The torsion angles between the perpendiculars to the coordination planes at aluminum and the sulfurs are 19.4 and 15.8° for $\text{Al}(1)$ and 22.5 and 21.8° for $\text{Al}(2)$. The $\text{Al}-\text{S}-\text{C}$ angles fall in the narrow range 101.2(1)–102.7(1)°.

$\text{Mes}_2\text{GaSMes}^*$ (**3**). A view of this molecule is shown in Figure 3. In the GaMes_2 moiety one Mes^* ring (C(19)) is oriented almost perpendicular (89.3°) to the $\text{SGa}(\text{C-}i\text{ps})_2$ least-squares plane whereas the averaged plane of the other ring (C(1)) lies almost perpendicular to the C(19) ring plane and its geometry is distorted in such a way that there is an angle of 42.2° between the C(ipso)-C(para) (i.e. the C(1)-C(4)) vector and the $\text{Ga}-\text{C}(1)$ bond. The methyl group of the GaSMes^* ($\text{Ga}-\text{S}-\text{C} = 102.9(3)^\circ$, $\text{Ga}-\text{S}$ distance = 2.271(2) Å) moiety is

Table 4. Important IR Stretching Frequencies (cm⁻¹) for the M–S(Thiolate) Bonds in Three- and Four-Coordinate Aluminum and Gallium Thiolates

compound	metal coordn. no.	ν , cm ⁻¹	ref
<i>n</i> -BuAl(SMes*) ₂ (1)	3	544	this work
<i>t</i> -BuAl(SMes*) ₂ (2)	3	524	this work
Al(SMes*) ₃	3	547	2
Mes* ₂ GaSMe (3)	3	343	this work
Mes* ₂ GaSPh (4)	3	333	this work
<i>n</i> -BuGa(SMes*) ₂ (5)	3	395	this work
Ga(SMes*) ₃	3	398	2
(<i>t</i> -Bu ₂ AlSTrip) ₂ (6)	4	418, 398, 362	this work
(THF)Al(STrip) ₃ (7)	4	475	this work
[Et ₂ GaSPh] ₂	4	325–315	28

to S(2) and S(3) are disposed on one side of the plane defined by the three sulfurs whereas the other is oriented on the opposite side. The Al–S–C angles also display variation. Thus, one angle, Al(1)–S(2)–C(16), is 98.8(2)°, whereas the others have almost equal values near 106°.

Spectroscopic Studies. In addition to the structural studies, the compounds were characterized by NMR and by IR spectroscopy. A listing of IR data for 1–7 and related compounds in the M–S stretching region is provided in Table 4. Variable-temperature NMR studies of 1–6 revealed significant dynamic behavior only in the cases of 3 and 4. In these compounds the ¹³C NMR signals due to the *o*-, *m*-, and *o*-*t*-Bu carbons were split into three separate peaks with a 2:1:1 intensity ratio at temperatures below –90 °C. Calculations¹⁷ showed that the barriers to the dynamic process involved were 9.7 ± 1.0 kcal mol⁻¹ for 3 and 8.9 ± 1.0 kcal mol⁻¹ for 4.

Discussion

The structural and spectroscopic work in this paper is based on the premise that, if M–S (M = Al or Ga) p–p π -bonding is significant, it should be detectable in the structural parameters and in M–S rotation barriers. Some of the expected structural effects may be illustrated by considering the series of compounds R₂MSR, R'M(SR)₂, and M(SR)₃. In the monothiolate there is a putative 1:1 interaction between the chalcogen lone pair and the formally empty metal p-orbital whereas in the di- and trithiolate the interaction is in a 1:2 or 1:3 ratio. Thus, the π -interaction in the M–S bonds of the series of compounds should become progressively weaker as thiolate substitution is increased. In addition to the trend in M–S bond lengths across the series of thiolate derivatives, the bond lengths may be compared to distances predicted from the sum of the radii.¹⁸ Experimental bond lengths that are shorter than the predicted values may be interpreted as supporting the existence of multiple bonding. It must be borne in mind, however, that the M–S bonds have significant ionic character and are thus subject to

correction for an ionic or resonance contribution to the bond strength. This correction is usually performed empirically and may lead to a quite substantial shortening in the M–S bond. Use of the empirical formulas of Schomaker and Stevenson^{19a} or Blom and Haaland^{19b} lead to the corrected bond lengths of 2.23 and 2.17 Å for Al–S and 2.21 and 2.18 Å for Ga–S. For comparison a summary of the most important structural data for compounds with bonding between three-coordinate aluminum or gallium and terminal ligands binding through sulfur is provided in Table 5. It can be seen that there are a total of seven compounds of this type for which data are currently available.

In spite of the limitations of this list, it can be seen that there are no trends in the structural parameters that would support the existence of significant π -bonding. The range of Al–S distances in the four aluminum compounds is 2.185(5)–2.195(2) Å. In other words, only one hundredth of an angstrom separates the longest and shortest averaged Al–S bond lengths. The difference is essentially insignificant since it is only twice the highest standard deviation. In addition, there is no apparent correlation between the Al–S distances and the torsion angle between the coordination planes at the aluminum and sulfur centers. Furthermore, the gallium thiolate species display a trend in Ga–S distances that is opposite to what is predicted on the basis of π -bonding. A similar, but much less pronounced, trend is discernible with Al–S compounds. It is notable, however, that the Ga–S distances in 5 and Ga(SMes*)₃² are almost equal whereas the Ga–S bond length in the monothiolate 3 is anomalously long. This lengthening may be due to the presence of two large Mes* substituents which may cause the Ga–S bond to lengthen for steric reasons. It is noteworthy in the case of 3 that there are close interactions between gallium and at least two hydrogens from ortho *t*-Bu groups from the C(19) ring so that the effective coordination number may be increased in this compound. Significantly, the Al–S and Ga–S bond lengths in Table 5 are very close to those predicted by the sum of the atomic radii, taking into account the empirical correction for ionic effects.^{17,18} The Ga–S distances are slightly longer than the Al–S distances even though the radius of gallium is slightly smaller than that of aluminum. This is because the ionic contribution which shortens the bond lengths is greater for aluminum owing to its greater electropositive character.²⁰ Other noteworthy features of the data in Table 5 are the variation in the torsion angle involving the M–S bonds, which bears no relationship to the M–S distance, and constancy of the M–E–C angles which are all within 3° of 100°.

In summary, the structural data in Table 5 do not support the existence of significant M–S π -bonding. The fact that the shortest average Al–S and Ga–S distances are observed for the trithiolates M(SMes*)₃² is more consistent with the progressive contraction of the effective radius of the metal with an increasing number of more electronegative substituents.²¹ Such a pattern is seen to a much greater degree in the more ionic aryloxy derivatives *t*-Bu₂AlO(2,6-*t*-Bu₂-4-MeC₆H₂)^{8a} (Al–O = 1.710(2) Å), MeAl{O(2,6-*t*-Bu-4-MeC₆H₂)₂}^{8b} (Al–O = 1.686(2) Å), and Al{O(2,6-*t*-Bu₂-4-MeC₆H₂)₃}^{8c} (Al–O = 1.648(7) Å).

The associated structure observed for (*t*-Bu₂AlSTrip)₂ (6) and the structure of the THF-coordinated species (THF)Al(STrip)₃ (7) underline the extreme tendency of aluminum thiolates to increase the metal coordination number by either association

(17) (a) DNMR simulations were carried out on an IBM 365 PC using the program DNMR5.^{17b} The rate constants for the coalescence temperature of the *o*-C and the *o*-C(CH₃)₃ signals were obtained by visually matching observed and calculated spectra. ΔG^\ddagger was calculated with the Eyring equation $\Delta G^\ddagger = -RT_c(\ln k(Nh/RT_c))$. (b) Stephenson, D. S.; Binsch, G. *QCPE* 1978, 11, 365.

(18) Radii of 1.3 Å for aluminum and 1.25 Å for gallium were used. These values are similar to those that can be expected from recent structural studies of three-coordinate compounds containing Al–Al and Ga–Ga bonds. For example Al–Al bond lengths of 2.660(1) and 2.647(3) Å have been reported: Uhl, W. *Z. Naturforsch.* 1988, 43B, 113. Wehmschulte, R. J.; Ruhlandt-Senge, K.; Olmstead, M. M.; Hope, H.; Sturgeon, B. E.; Power, P. P. *Inorg. Chem.* 1993, 32, 2983. Similarly, Ga–Ga bond lengths of 2.541(1) and 2.515(3) Å were reported: Uhl, W.; Layh, M.; Hildenbrand, T. *J. Organomet. Chem.* 1989, 364, 289. He, X.; Bartlett, R. A.; Olmstead, M. M.; Ruhlandt-Senge, K.; Sturgeon, B. E.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* 1993, 32, 717. A radius of 1.02 Å was used for sulfur.

(19) (a) Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* 1941, 63, 37. (b) Blom, R.; Haaland, A. *J. Mol. Struct.* 1985, 129, 1.

(20) In the calculations Allred–Rochow radii which give EN values of 1.4 and 1.8 for Al and Ga were used.

(21) Haaland, A. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH: New York, 1993; Chapter 1.

Table 5. Important Structural Data for Compounds Involving Bonding between Three-Coordinate Aluminum or Gallium and Sulfur Ligands

compound	M-E, Å	M-E-C, deg	torsion angle, deg	ref
<i>n</i> -BuAl(SMes*) ₂ (1)	2.191(4)	97.2(1.2)	2.5, 2.6, 12.6, 17.5	this work
<i>t</i> -BuAl(SMes*) ₂ (2)	2.195(2)	102.4(5)	15.8, 19.4, 21.8, 22.5	this work
Al(SMes*) ₃	2.185(5)	100.4(1.4)	8.5, 14.0, 39.9	2
S[Al{CH(SiMe ₃) ₂ } ₂] ₂	2.187(4)	117.5(3) ^a	39.9	6
Mes* ₂ GaSMe (3)	2.271(2)	102.9(3)	5.8	this work
<i>n</i> -BuGa(SMes*) ₂ (5)	2.186(8)	97.6 (1.0)	1.2, 1.7, 8.0, 12.9	this work
Ga(SMes*) ₃	2.205 (6)	100.4(8)	10.6, 13.6, 37.3	2

^a S-M-S angle.

or by adduct formation with Lewis bases. The bridging Al-S distances in **6** are almost 0.2 Å longer than the Al-S bond lengths observed for the three-coordinate compounds. They are, however, comparable to the range of Al-S bond distances (*ca.* 2.35–2.40 Å) observed in other associated aluminum thiolates.¹ The dimeric structure of **6** may also be contrasted to the trimeric structures of [Me₂Al(SC₆H₄-2-R)]₃ (Al-S = 2.35 and 2.36 Å; R = *i*-Pr²² or *t*-Bu²³) and (*i*-Bu₂AlSTrip)₃²² (Al-S = 2.37 Å). The lower association number and slightly longer average Al-S distances observed in **6** are attributable to the higher steric demands of the *t*-Bu aluminum substituents.

The synthesis and structural investigation of compound **7** arose during attempts to isolate a three-coordinate aluminum thiolate with less bulky substituents than Mes*. Failure to grow crystals of Al(STrip)₃ led to attempts to grow derivatized crystalline species. When THF was introduced to the solvent system during syntheses, the adduct (THF)Al(STrip)₃ (**7**), which crystallized readily, was isolated. The structure of **7**, which is the first of its kind to be determined for an aluminum thiolate, has distorted tetrahedral coordination at aluminum with the angles between the thiolate ligands being considerably wider than those between the THF and thiolate ligands. However, there is also much variation in the S-Al-S angles and in the Al-S-C angles. Most probably, steric interactions in the coordination sphere play an important role in determining these. The average Al-S bond length, 2.227(6) Å, is only *ca.* 0.09 Å longer than that observed for Al(SMes*)₃. The small increase between the three- and four-coordinate complexes is similar to that observed in the case of gallium analogues where the Ga-S distances in [Ga(SET)₄]⁻²⁴ (2.264(3) Å) and [Ga(SPh)₄]⁻²⁴ (2.257(8) Å) are only *ca.* 0.05 Å longer than the 2.205(6) Å seen in Ga(SMes*)₃.² The fact that Al(STrip)₃ forms a strong complex with THF (and with excess LiSTrip to give LiAl(STrip)₄)²⁵ is of course indirect evidence for the weakness of Al-S π-bonding. Presumably, if delocalization of the sulfur lone pairs into the aluminum p-orbital were significant, complex **7** would not readily form owing to the reduction in the Lewis acidity of the aluminum center.

Spectroscopic studies of **1–5** are in agreement with the conclusions drawn from the structural data. Variable-temperature NMR studies of **1**, **2**, and **5** and the trithiolate species M(SMes*)₃ do not show any dynamic behavior in the temperature range -90 to +25 °C, indicating that barriers to rotation around the M-S bonds are small and probably less than 8–9 kcal mol⁻¹. This may be contrasted with the lighter analogue B-S bonds which have rotational barriers as high as 18 kcal mol⁻¹.²⁶ Dynamic behavior was observed in the cases of **3** and **4**, and the energy barriers were estimated¹⁷ for these compounds,

9.7 ± 1.0 and 8.9 ± 1.0 kcal mol⁻¹, should be regarded as the upper limits for any possible π-interaction. It is more probable that the barriers observed in **3** or **4** are a consequence of the steric effects of the two large Mes* substituents at gallium. A dynamic process involving the "linear inversion" of the M-S-R moiety is unlikely since calculations on the related B-S-R system indicates that this process is more energy demanding than rotation around the B-S in a bent B-S-R moiety.^{26b} It is apparent from the structure of **3** that the -SMe substituent is oriented such that the methyl group is in the Z-configuration with respect to the C(19) Mes* ring substituent which, being oriented almost perpendicular to the coordination plane at gallium, offers the least steric interference. Rotating the sulfur methyl group through 180° would result in much greater steric interference with the *t*-Bu groups of the C(1) Mes* ring, which adopts an orientation that places the *t*-Bu groups much closer to the gallium coordination plane.²⁷ The observation of the 2:1:1 signal intensity ratio for the ortho, meta, and ortho *t*-Bu carbons apparently requires that the molecule be locked in approximately the same conformation depicted in Figure 3. Steric effects probably also account for the dynamic behavior in the ¹H NMR spectrum of {(Me₃Si)₂CH}₂GaTeSi(SiMe₃)₃.⁵

The IR spectra for **1–5** (Table 4) show bands that are attributable to M-S stretches. It should be borne in mind, however, that these M-S stretches are probably coupled to the C-S vibrations. The bands for the three-coordinate complexes occur at considerably higher frequencies than those of the four-coordinate compounds. The bands for the three-coordinate aluminum species **1**, **2**, and Al(SMes*)₃² occur within a relatively narrow range, and the Ga-S stretching frequencies for **5** and Ga(SMes*)₃ are almost identical. The Ga-S bands of **3** and **4** occur at significantly lower frequencies, in keeping with their longer Ga-S distances and weaker Ga-S bonds. The four-coordinate gallium and aluminum complexes also show substantial decreases in their stretching frequencies, in harmony with their longer Al-S distances.

Conclusion

Although the number of three-coordinate aluminum and gallium thiolates is currently quite limited, it may be tentatively concluded that π-bonding involving p-orbital overlap between these metals and sulfur is weak and has an upper limit of 8–9 kcal mol⁻¹ in the compounds examined in this paper.

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Supplementary Material Available: Tables giving full data collection parameters and further details of refinement, atomic coordinates and equivalent isotropic thermal parameters, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters (68 pages). Ordering information is given on any current masthead page.

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