Organometallics **1995,** *14,* 2903−2917

Organoaluminum and -gallium Thiolates. 1. Synthetic and X-ray Structural Studies

Majid Taghiof, Mary Jane Heeg, Marcia Bailey, David G. Dick, Rajesh Kumar,
D. Greg Hendershot, Hamid Rahbarnoohi, and John P. Oliver*

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received February 27, 1995[⊗]

Organoaluminum and -gallium thiolates are prepared in high yield by the reaction of triorganoaluminum and -gallium derivatives with thiols. In this way, $[Mes_2Al(\mu\text{-}SBz)]_2$ (Mes = 2,4,6-$Me_3C_6H_2$; Bz = $CH_2C_6H_5$) (**1**), $[Me_2Al(\mu\text{-}SSiPh_3)]_2$ (**2**), $[Mes_2Al(\mu\text{-}SPh)]_2$ (**3**), $\{Me_2Al[\mu\text{-}S(2\text{-}t\text{-}BuC_6H_4)]\}_3$ (**4**), $\{Me_2Al[\mu\text{-}S(2\text{-}Me_3Si)C_6H_4]\}_3$ (**5**), $\{Me_2Al[\mu\text{-}S(2\text{-}i\text{-}PrC_6H_4)]\}_3$ (**6**), $\{i\text{-}Bu_2Al[\mu\text{-}S(2,4,6\text{-}i\text{-}Pr_3C_6H_2)]\}_3$ (**7**), $\{Me_2Al[\mu\text{-}S(2,6\text{-}Me_2C_6H_3)]\}_4$ (**8**), and $\{Me_2Ga[\mu\text{-}S(2,6\text{-}Me_2C_6H_3)]\}_4$ (**9**) were prepared and crystallographically characterized. The dimethyl- and dimesitylaluminum thiolates **1**−**3** were determined to be dimeric with four-membered $(AlS)_2$ rings. The structure of **1** was determined in space group $P2_1/n$ (No. 14): a = 10.660(4) Å, b = 12.268(2) Å, c = 17.793(3) Å, β = 106.94(2)°, Z = 4, R = 6.7%, and R_w = 6.1%. The structures of **2** and **3** were determined in space group $P\bar{1}$ (No. 2): a = 9.077(2) Å, b = 13.847(3) Å, c = 16.724(4) Å, α = 101.08(2)°, β = 95.34(2)°, γ = 103.38(2)°, Z = 2 (dimers), R = 5.2%, and R_w = 5.1% for **2**, and a = 11.068(5) Å, b = 12.470(3) Å, c = 17.654(5) Å, α = 90.97(2)°, β = 107.77(3)°, γ = 112.23(3)°, Z = 4, R = 5.9%, and R_w = 4.8% for **3**. The dialkylaluminum thiolates, **4**−**7**, were found to be trimeric in the solid state. The structure of **4** was determined in space group $P2_1/c$ (No. 14), a = 9.324(7) Å, b = 18.632(5) Å, c = 23.959(9) Å, β = 98.31(5)°, Z = 4 (trimers), R = 7.6%, and R_w = 5.2%; **5** in space group $P\bar{1}$ (No. 2), a = 10.149(4) Å, b = 14.427(5) Å, c = 15.159(4)Å, α = 88.19(3)°, β = 89.39(3)°, γ = 88.57(3)°, Z = 2 (trimers), R = 5.0%, and R_w = 5.0 %; **6** in space group $P\bar{1}$ (No. 2), a = 12.538(5) Å, b = 13.180(2) Å, c = 13.873(2) Å, α = 74.38(1)°, β = 64.18(2)°, γ = 69.44(2)°, Z = 2 (trimers), R = 5.2% and R_w = 4.4%; and **7** in space group $P2_1/c$ (No. 14), a = 13.935(2) Å, b = 22.563(4) Å, c = 25.044(4) Å, β = 101.44(1)°, Z = 4 (trimers), R = 12.5%, and R_w = 14.2%. The sulfur atoms in **7** are in a planar environment. Compounds **8** and **9** are tetrameric with eight-membered $(MS)_4$ (M = Al, Ga) ring systems. They are isomorphous, and their structures were determined in space group $P\bar{1}$ (No. 2). For **8** a = 8.555(1) Å, b = 11.869(1) Å, c = 12.688(1) Å, α = 96.546(8)°, β = 106.34(1)°, γ = 109.06(1)°, Z = 2, R = 5.0%, and R_w = 5.2%, and for **9** a = 8.525(2) Å, b = 11.805(3) Å, c = 12.714(4) Å, α = 96.36(2)°, β = 106.46(2)°, γ = 108.90(2)°, Z = 2, R = 6.1%, and R_w = 6.6%.

Introduction

The structural features of group 13 organometallic compounds have been of fundamental interest because of the three-center, two-electron bonds that are commonly observed in these systems.[1] When diorgano−group 13 pnictinides or chalcogenides are prepared, these electron-deficient bonds are replaced by normal two-electron bonds, giving rise to a new series of compounds with similar structures but differing electronic properties because of the electron-rich bridging atoms.

Earlier work has been reviewed by Matteson,[2] Coates,[3] Eisch,[4] and Mole.[5] Extensive reviews of these topics in "Coordination Chemistry of Aluminum"[6] provide detailed information on the structures, bonding, and reactivity of Group 13−15 and Group 13−16 compounds. We have recently reviewed the work on the thiolates, selenolates, and tellurolates of group 13 derivatives.[7,8]

These compounds exhibit a variety of structural types depending on the metal, the chalcogen, and the substituents on each. The derivatives with very bulky substituents are monomeric with the substituents surrounding the metal atom preventing dimerization. These include the oxygen derivatives, $MeAl[2,6\text{-}(t\text{-}Bu)_2\text{-}4\text{-}MeC_6H_2O]_2$[9] and $(t\text{-}Bu)_2GaOCPh_3$,[10] the sulfur derivatives, $Al(SMes^*)_3$ and $Ga(SMes^*)_3$ (Mes* = 2,4,6-t-Bu_3-C_6H_2),[11] the selenium derivative, $Ga(SeMes^*)_3$,[12] and the tellurium compound, $[(Me_3Si)_2CH]_2GaTeSi(SiMe_3)_3$.[13]

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1995.

[1] Oliver, J. P. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; John Wiley and Sons: New York, 1985; Vol. 2, pp 789−826.

[2] Matteson, D. S. *Organometallic Reaction Mechanisms*; Academic Press: New York, 1974.

[3] Coates, G. E.; Wade, K. *The Main Group Elements* 3rd ed.; Methuen: London, 1967; Vol. 1.

[4] Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 1, pp 555−683.

[5] Mole, T.; Jeffrey, E. A. *Organoaluminum Compounds*; Elsevier: Amsterdam, 1972.

[6] Robinson, G. H. *Coordination Chemistry of Aluminum*; VCH: New York, 1993.

[7] Oliver, J. P.; Kumar, R. *Polyhedron* **1990**, *9*, 409.

[8] Oliver, J. P.; Kumar, R.; Taghiof, M. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH: New York, 1993; pp 167−195.

[9] Robinson, G. H.; Sangokoya, S. A. *J. Am. Chem. Soc.* **1987**, *109*, 6862.

[10] Cleaver, W. M.; Barron, A. R. *Organometallics* **1993**, *12*, 1001.

0276-7333/95/2314-2903$09.00/0

The dimeric derivatives, $[R_2M(\mu\text{-}ER')]_2$ (R and R′ = alkyl, aryl; M = Al, Ga, In; E = O, S, Se, Te) constitute a second class of structures. In addition to the alkoxides which have been studied extensively, these include $[Me_2Al(\mu\text{-}SC_6F_5)]_2$,[14] $[(t\text{-}Bu)_2Al(\mu\text{-}Te\text{-}t\text{-}Bu)]_2$,[15] $[Ph_2Ga(\mu\text{-}SEt)]_2$,[16] $[t\text{-}Bu_2Ga(\mu\text{-}SH)]_2$,[17] $[Ph_2Ga(\mu\text{-}SSn(C_6H_{11})_3]_2$,[18] $[Ph_2Ga(\mu\text{-}SeMe)]_2$,[19] and $[Np_2Ga(\mu\text{-}TePh)]_2$.[20] These examples all have planar or nearly planar $(ME)_2$ rings with the substituent on the chalcogen in the *trans* configuration.

The third class of compounds are those which involve six-membered $(ME)_3$ rings, but there are very few examples with chalcogens. The reported structures include $[Me_2Al(\mu\text{-}OMe)]_3$[21] and $[Me_2In(\mu\text{-}SSiPh_3)]_3$.[22] There also is an unusual sulfide derivative, $[(t\text{-}Bu)(Py)Ga(\mu\text{-}S)]_3$.[23] For Group 13−15 derivatives, there are a number of examples of $[R_2M(\mu\text{-}ER'_2)]_3$ (E = N, P, As; R = H, Me, Ph).[24−28] No trimeric derivatives of aluminum or gallium with thiolate, selenolate, or tellurolate bridges have been reported. The only two eight-membered ring systems that have been reported for group 13 derivatives are $[Me_2Al(\mu\text{-}F)]_4$[29] with bridging fluorine atoms between the Me_2Al units and $[Me_2Ga(\mu\text{-}OH)]_4$[30] with bridging hydroxyl groups.

Other studies have provided isolated examples of chains such as $[Me_2Al(\mu\text{-}SMe)]_\infty$,[31] $[MeIn(SePh)(\mu\text{-}SePh)]_\infty$,[32] and $[In(SePh)_3]_\infty$.[33] Small heteronuclear cluster compounds, including $[t\text{-}BuGa(\mu_3\text{-}S)]_4$[15,34] and $[t\text{-}BuGa(\mu_3\text{-}S)]_6$,[23] have been reported with sulfide bridging groups.

The studies reported do not provide adequate data to develop an understanding of those factors which determine the aggregate size or structure for the group 13−16 organometallic derivatives of the type $[R_2M(\mu\text{-}ER')]_n$. To address this problem, we have started a systematic study of the syntheses and structures of these derivatives and in this paper present our findings on a series of dialkylaluminum thiolates with four-membered $(AlS)_2$, six-membered $(AlS)_3$, and eight-membered $(AlS)_4$ rings and an example of a gallium thiolate with an eight-membered $(GaS)_4$ ring. A detailed study of the equilibria and the dynamic behavior of these systems in solution as followed by NMR spectroscopy will be discussed in a subsequent paper.[35]

Experimental Section

General Data. The compounds synthesized are both air and moisture sensitive, so they were prepared and manipulated under an argon atmosphere using standard Schlenk line and glovebox techniques. Argon was purified by passing it through a series of columns containing Deox catalyst (Alfa), calcium sulfate, and phosphorus pentoxide. All solvents used were dried using standard techniques,[36] and all glassware was oven- or flame-dried. Trimethylaluminum (2.0 M in toluene), $i\text{-}Bu_3Al$ (1.0 M in toluene), decalin, 2-bromomesitylene, 2-isopropylthiophenol, benzylthiol, benzenethiol, 2,6-dimethylthiophenol, and 2,4,6-triisopropylbenzenesulfonyl chloride were purchased from Aldrich and used without further purification. Me_3Ga was obtained from Strem, and 2-*t*-butylthiophenol was obtained from Lancaster. $2\text{-}(Me_3Si)C_6H_4SH$,[37] Ph_3SiSH,[38] and Mes_3Al (Mes = $2,4,6\text{-}Me_3C_6H_2$)[39] were prepared according to published procedures. ^1H and ^{13}C NMR spectra were recorded on a General Electric QE300 or GN300 NMR spectrometer at ambient temperature. The proton chemical shifts were referenced to C_6D_5H (δ = 7.15 ppm), the carbon resonances to C_6D_6 (δ = 128.0 ppm), and the ^{29}Si NMR spectra (59.60 MHz) to $Si(CH_3)_4$ (δ = 0 ppm) in benzene. Analyses were performed at Galbraith Laboratories, Knoxville, TN. Melting points were measured on a Haake-Buchler melting point apparatus and are uncorrected. Mass spectrometry data were obtained on a Kratos MS80 RFA mass spectrometer using electron ionization (70 eV).

Synthesis of $\mathbf{2,4,6\text{-}\mathit{i}\text{-}Pr_3C_6H_2SH}$. The thiol, $2,4,6\text{-}i\text{-}Pr_3C_6H_2SH$, was prepared as described previously and purified by distillation under reduced pressure.[40] ^1H NMR (C_6D_6): 1.196 (d, J_{H-H} = 6.9 Hz, 12H, $2,6\text{-}CH(C\mathbf{H}_3)_2$), 1.199 (d, J_{H-H} = 6.6 Hz, 6H, $4\text{-}CH(C\mathbf{H}_3)_2$), 2.79 (sept, 1H, $4\text{-}C\mathbf{H}(CH_3)_2$), 2.90 (s, 1H, SH), 3.52 (sept, 2H, $2,6\text{-}C\mathbf{H}(CH_3)_2$), 7.05 (s, 2H, aryl H). $^{13}C\{^1H\}$ NMR (C_6D_6): 23.4, 24.3 ($CH(\mathbf{C}H_3)_2$), 32.2, 34.6 ($\mathbf{C}H(CH_3)_2$), 121.5, 124.8, 147.3, 148.5 (aryl).

Synthesis of $\mathbf{[Mes_2Al(\mu\text{-}SBz)]_2}$ (1). Benzylthiol (Bz = $CH_2C_6H_5$) (0.3 mL, 2.55 mmol) was added dropwise to a solution of Mes_3Al (Mes = $2,4,6\text{-}Me_3C_6H_2$) (1.0 g, 2.6 mmol) in 50 mL of toluene. The product precipitated from the reaction mixture and was recrystallized from warm toluene. Yield: ~60%. MP: 279−280 °C. ^1H NMR (C_6D_6, δ, ppm): 2.13 (s, 6H, $4\text{-}CH_3$ of Mes), 2.66 (s, 12H, $2,6\text{-}CH_3$ of Mes), 3.56 (s, 2H, $SC\mathbf{H}_2Ph$), 6.72 (s, 2H, H of Mes), 6.78 (m, 3H, $SCH_2\mathbf{Ph}$), 6.90 (m, 2H, $SCH_2\mathbf{Ph}$). ^{13}C NMR (C_6D_6, δ, ppm): 21.2 ($4\text{-}CH_3$ of Mes), 26.0 ($2,6\text{-}CH_3$ of Mes), 36.1 ($S\mathbf{C}H_2Ph$), 127.3, 128.9, 138.4, 138.7, 145.7 (aryl). Anal. for $C_{25}H_{29}AlS$. Calcd (found): C, 77.28 (75.62); H, 7.52 (7.48).

---

(11) Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 2633.

(12) Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 3683.

(13) Uhl, W.; Layh, M.; Becker, G.; Klinkhammer, K. W.; Hildenbrand, T. *Chem. Ber.* **1992**, *125*, 1547.

(14) de Mel, V. S. J.; Kumar, R.; Oliver, J. P. *Organometallics* **1990**, *9*, 1303.

(15) Cowley, A. H.; Jones, R. A.; Harris, P. R.; Atwood, D. A.; Contreras, L.; Burek, C. J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1143.

(16) Hoffmann, G. G.; Burschka, C. *J. Organomet. Chem.* **1984**, *267*, 229.

(17) Power, M. B.; Barron, A. R. *J. Chem. Soc., Chem. Commun.* **1991**, 1315.

(18) Ghazi, S. U.; Heeg, M. J.; Oliver, J. P. *Inorg. Chem.* **1994**, *33*, 4517.

(19) Kumar, R.; Dick, D. G.; Ghazi, S. U.; Taghiof, M.; Heeg, M. J.; Oliver, J. P. *Organometallics* **1995**, *14*, 1601.

(20) Banks, M. A.; Beachley, O. T., Jr.; Gysling, H. J.; Luss, H. R. *Organometallics* **1990**, *9*, 1979.

(21) Drew, D. A.; Haaland, A.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1973**, *398*, 241.

(22) Rahbarnoohi, H.; Taghiof, M.; Heeg, M. J.; Dick, D. G.; Oliver, J. P. *Inorg. Chem.* **1994**, *33*, 6307.

(23) Power, M. B.; Ziller, J. W.; Barron, A. R. *Organometallics* **1992**, *11*, 2783.

(24) Beachley, O. T., Jr.; Royster, T. L., Jr.; Arhar, J. R.; Rheingold, A. L. *Organometallics* **1993**, *12*, 1976.

(25) McLaughlin, G. M.; Sim, G. A.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1972**, 2197.

(26) Semenenko, K. N.; Lobkovskii, E. B.; Dorosinskii, A. L. *J. Struct. Chem. (Engl. Transl.)* **1972**, *13*, 743.

(27) Harrison, W.; Storr, A.; Trotter, J. *J. Am. Chem. Soc., Dalton Trans.* **1972**, 1554.

(28) Cowley, A. H.; Jones, R. A.; Kidd, K. B.; Nunn, C. M.; Westmoreland, D. L. *J. Organomet. Chem.* **1988**, *341*, C1.

(29) Gunderson, G.; Haugen, T.; Haaland, A. *J. Organomet. Chem.* **1973**, *54*, 77.

(30) Smith, G. S.; Hoard, J. L. *J. Am. Chem. Soc.* **1959**, *81*, 3907.

(31) Brauer, D. J.; Stucky, G. D. *J. Am. Chem. Soc.* **1969**, *91*, 5462.

(32) Rahbarnoohi, H.; Kumar, R.; Heeg, M. J.; Oliver, J. P. *Organometallics*, in press.

(33) Annan, T.; Kumar, R.; Mabrouk, H. E.; Tuck, D. G.; Chadha, R. K. *Polyhedron* **1989**, *8*, 865.

(34) Power, M. B.; Ziller, J. W.; Tyler, A. N.; Barron, A. R. *Organometallics* **1992**, *11*, 1055.

(35) Kumar, R.; Bailey, M.; Barber, M.; Hendershot, D. G.; Taghiof, M.; Rahbarnoohi, H.; Dick, D. G.; Oliver, J. P. To be submitted for publication.

(36) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*; John Wiley & Sons: New York, 1986.

(37) Block, E.; Eswarakrishnan, V.; Gernon, M.; Ofori-Okai, G.; Saha, C.; Tang, K.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 658.

(38) Calas, R.; Duffaut, N.; Martel, B.; Paris, C. *Bull. Soc. Chim. Fr.* **1961**, 886.

(39) Seidel, W. *Z. Anorg. Allg. Chem.* **1985**, *524*, 101. Jerius, J. T.; Hahn, J. M.; Rahman, A. F. M. M.; Mols, O.; Ilsley, W. H.; Oliver, J. P. *Organometallics* **1986**, *5*, 1812.

(40) Pearson, D. E.; Caine, D.; Field, L. *J. Org. Chem.* **1960**, *25*, 867.

Synthesis of $[Me_2Al(\mu\text{-}SSiPh_3)]_2$ (2). Me_3Al (2.0 mL, 4.00 mmol) was added at room temperature to Ph_3SiSH (1.00 g, 3.42 mmol) in pentane. Gas evolution was noted during the course of the reaction. The product precipitated and subsequently was recrystallized from a pentane/toluene mixture at room temperature resulting in X-ray quality crystals. Yield: ~70%. MP: 195 °C. ^1H NMR (C_6D_6, δ, ppm): −0.56 (s, trimer), −0.45 (s, $Al(CH_3)_2$, dimer). (An equilibrium for the process 2 trimer $\rightleftharpoons$ 3 dimer is established with K_{eq} = 31 mol/L. Details are discussed elsewhere.[35]) 7.04 (m, 9H, Ph), 7.74 (m, 6H, Ph). ^{13}C NMR (C_6D_6, δ, ppm): −4.36, −3.12 ($Al(CH_3)_2$), 128.3, 128.5, 130.7, 130.8, 133.5, 133.7, 136.1, 136.6 (aryl). ^{29}Si NMR (C_6D_6, δ, ppm): −2.2, −1.7 ($SiPh_3$). Anal. for $C_{20}H_{21}AlSiS$. Calcd (found): C, 68.94 (69.23%); H, 6.01% (5.65%).

Synthesis of $[Mes_2Al(\mu\text{-}SPh)]_2$ (3). Compound **3** was prepared by reaction of PhSH (8.4 mL, 0.195 M, 1.63 mmol) with Mes_3Al (0.630 g, 1.64 mmol) in hexane as described for **2**. This material was recrystallized from hot hexane/toluene (50:50 solution), resulting in X-ray quality crystals. Yield: 24%. MP: 233 °C. ^1H NMR (C_6D_6, δ, ppm): 2.03 (s, 6H, 4-CH_3 of Mes), 2.74 (s, 12H, 2,6-CH_3 of Mes), 6.51 (m, 3H, Ph), 6.56 (s, 4H, aryl of Mes), 6.98 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): 21.1 (4-CH_3 of Mes), 25.6 (2,6-CH_3 of Mes), 127.9, 129.1, 133.9, 134.3, 138.0, 145.29. MS (EI, *m/e*): 483 ($Mes_2Al(SPh)_2$, 0.1), 438 ($Mes_2Al(SPh)_2$ − 3Me, 1.0).

Synthesis of $\{Me_2Al[\mu\text{-}S(2\text{-}t\text{-}BuC_6H_4)]\}_3$ (4). Compound **4** was prepared by reaction of Me_3Al (2.5 mL, 2.0 M soln) with 2-*tert*-butylthiophenol as described for **2**. The solid was recrystallized from pentane at −10 °C. Yield: ~60%. MP: 171 °C. ^1H NMR (C_6D_6, δ, ppm): −0.43 (s, 3H, $Al(CH_3)_2$), −0.23 (s, 6H, $Al(CH_3)_2$), −0.11 (s, 6H, $Al(CH_3)_2$), 0.19 (s, 3H, $Al(CH_3)_2$), 1.55 (s, 9H, *t*-Bu), 1.53 (s, 18H, *t*-Bu), 6.98 (m, 6H, Ar), 7.94 (m, 2H, Ar), 7.26 (m, 3H, Ar), 8.13 (m, 1H, Ar). $^{13}C\{^1H\}$ NMR (C_6D_6, δ, ppm): −8.1 ($Al(CH_3)_2$), −7.2 ($Al(CH_3)_2$), −5.5, ($Al(CH_3)_2$), 30.7 ($C(CH_3)$), 30.7 ($C(\mathbf{C}H_3)$), 36.5 ($\mathbf{C}(CH_3)$), 125.4, 126.6, 128.2, 128.7, 138.0, 138.6, 139.1, 152.3, 152.4 (aryl). Anal. for $C_{12}H_{19}AlS$. Calcd (found): C, 64.83 (61.87); H, 8.61 (7.98).

Synthesis of $\{Me_2Al[\mu\text{-}S(2\text{-}Me_3Si)C_6H_4]\}_3$ (5). Compound **5** was prepared by reaction of the thiol, $HS(2\text{-}Me_3Si)C_6H_4$ (0.60 mL, 3.4 mmol), with Me_3Al (1.7 mL, 2.0 M solution, 3.4 mmol) following the procedure used for **2**. The white solid was recrystallized from pentane, yielding colorless crystals. Yield: ~60%. MP: 169 °C. ^1H NMR (C_6D_6, δ, ppm): −0.42 (s, 3H, $Al(CH_3)_2$-trimer), −0.34 (s, 6H, $Al(CH_3)_2$-trimer), −0.15 (s, 12H, $Al(CH_3)_2$-dimer), −0.05 (s, 6H, $Al(CH_3)_2$-trimer), 0.13 (s, 3H, $Al(CH_3)_2$-trimer), 0.42 (s, 18H, $SiMe_3$-dimer), 0.43 (s, 9H, $SiMe_3$-trimer), 0.44 (s, 18H, $Si(CH_3)_3$-trimer) (An equilibrium for the process 2 trimer $\rightleftharpoons$ 3 dimer is established with K_{eq} = 0.4 mol/L. Details are discussed elsewhere.[35], 7.01 (m, 5H, aryl), 7.21 (d of t, J_{H-H} = 7.2 and 1.5 Hz, 1H, aryl), 7.39 (d of d, 3H, J_{H-H} = 1.2 and 7.2 Hz, aryl), 7.87 (d, J_{H-H} = 6.9 Hz, 2H, aryl), 8.06 (d, J_{H-H} = 7.8 Hz, 1H, aryl). ^{13}C NMR (C_6D_6, δ, ppm): −7.9, −7.3, −6.8, −5.4, ($Al(CH_3)_2$), 0.7, 0.3 ($Si(CH_3)_3$-trimer), 0.01 ($Si(CH_3)_3$-dimer), 127.1 127.4, 129.3, 130.1, 130.3, 133.1, 133.3, 135.0, 136.0, 136.2, 136.5, 136.9, 145.3, 145.5 (aryl of dimer and trimer). Anal. for $C_{11}H_{19}AlSSi$. Calcd (found): C, 55.42 (51.97), H, 8.03 (7.76).

Synthesis of $\{Me_2Al[\mu\text{-}S(2\text{-}i\text{-}PrC_6H_4)]\}_3$ (6). Trimethylaluminum (3.5 mL, 2.0 M soln, 7.0 mmol) was added to 1.0 mL (6.89 mmol) of 2-isopropylthiophenol in approximately 50 mL of pentane. Colorless crystals were obtained from the solution by cooling to −10 °C. Yield: ~50%. MP 125 °C. ^1H NMR (C_6D_6, δ, ppm): −0.17 (s, 6H, $Al(CH_3)_2$), 1.13 (d, J_{H-H} = 7 Hz, 6H, $\text{-}CH(C\mathbf{H}_3)_2$), 3.80 (sept, J_{H-H} = 7 Hz, 1H, $\mathbf{CH}(CH_3)_2$), 7.00 (m, 3H, Ar), 7.91 (m, 1H, Ar). ^{13}C NMR (C_6D_6, δ, ppm): −7.6 ($Al(CH_3)_2$), 23.0 ($\text{-}CH(CH_3)_2$), 31.3 ($\text{-}CH(CH_3)_2$), 124.9, 126.5, 126.8, 129.1, 135.6, 151.8 (aryl). Anal. for $C_{11}H_{17}AlS$. Calcd (found): C, 63.43 (61.56); H, 8.23 (7.76).

Synthesis of $\{i\text{-}Bu_2Al[\mu\text{-}S(2,4,6\text{-}i\text{-}Pr_3C_6H_2)]\}_3$ (7). Compound **7** was prepared by reaction of triisobutylaluminum (5.0 mL, 1.0 M soln, 5.0 mmol) with 2,4,6-triisopropylthiophenol (1.0 mL, 4.45 mmol) by the procedure used for **2**. Cooling the pentane solution to −10 °C produced crystals. Yield: ~30%. MP: 107 °C. ^1H NMR (C_6D_6, δ, ppm): 0.73 (d, J_{H-H} = 6.9 Hz, 4H, $Al\text{-}C\mathbf{H}_2CH(CH_3)_2$), 0.89 (d, J_{H-H} = 6.3 Hz, 12H, $Al\text{-}CH_2CH(C\mathbf{H}_3)_2$), 1.13 (d, J_{H-H} = 6.6 Hz, 6H, 2,6-$CH(C\mathbf{H}_3)_2$), 1.51 (d, J_{H-H} = 6.3 Hz, 12H, 4-$CH(C\mathbf{H}_3)_2$), 1.93 (sept, J_{H-H} = 6.8 Hz, 2H, $Al\text{-}CH_2C\mathbf{H}(CH_3)_2$), 2.70 (sept, J_{H-H} = 6.9 Hz, 1H, 4-$C\mathbf{H}(CH_3)_2$), 4.30 (sept, J_{H-H} = 6.8 Hz, 2H, 2,6-$C\mathbf{H}(CH_3)_2$), 7.13 (s, 2H, aryl). ^{13}C NMR (C_6D_6, δ, ppm): 23.9, 24.8, 25.7, 25.9, 28.2, 32.5, 34.3, 122.5, 123.1, 149.8, 153.1. Anal. for $C_{23}H_{41}AlS$. Calcd (found): C, 73.35 (68.61); H, 10.97 (10.08).

Synthesis of $\{Me_2Al[\mu\text{-}S(2,6\text{-}Me_2C_6H_3)]\}_4$ (8). Compound **8** was prepared by the procedure used for **2** by addition of 2,6-dimethylthiophenol (1.0 mL, 7.51 mmol) to Me_3Al (3.75 mL, 2.0 M solution, 7.5 mmol). The reaction mixture stood at −20 °C for 24 h during which time crystalline **8** deposited. Yield: 90%. MP: 140−143 °C. ^1H NMR (C_6D_6, δ, ppm): −0.30 (s, 6H, $Al(CH_3)_2$-trimer), −0.23 (s, 6H, $Al(CH_3)_2$-dimer), 2.60 (s, 6H, 2,6-$(C\mathbf{H}_3)_2C_6H_3$-trimer), 2.60 (s, 6H, 2,6-$(C\mathbf{H}_3)_2C_6H_3$-dimer), 6.85 (s, 3H, 2,6-$(CH_3)_2C_6\mathbf{H}_3$-trimer), 6.87 (s, 3H, 2,6-$(CH_3)_2C_6\mathbf{H}_3$-dimer). (An equilibrium for the process 2 trimer $\rightleftharpoons$ 3 dimer is established with K_{eq} = 0.6 mol/L. Details are discussed elsewhere.[35]) ^{13}C NMR (C_6D_6, δ, ppm): −6.7 ($Al(CH_3)_2$), −6.2 ($Al(CH_3)_2$), 24.0 (2,6-$(\mathbf{C}H_3)_2C_6H_3$), 24.3 (2,6-$(\mathbf{C}H_3)_2C_6H_3$), 128.2, 128.3, 128.8, 128.9, 142.5, 142.7, (aryl). MW (cryoscopically in benzene): 0.1976 g of **8** in 5.244 g of benzene, ΔT = 0.340 °C, MW = 567, *n* = 2.92; 0.468 g of **8**, in 5.681 g of benzene, ΔT = 0.763 °C, MW = 574, *n* = 2.96; calcd for trimer, 583.2. Anal. for $C_{10}H_{15}AlS$. Calcd (found): C, 61.83 (60.83); H, 7.78 (7.78).

Synthesis of $\{Me_2Ga[\mu\text{-}S(2,6\text{-}Me_2C_6H_3)]\}_4$ (9). Trimethylgallium (0.36 mL, 3.62 mmol) was added to 0.500 g (0.48 mL, 3.62 mmol) of 2,6-dimethylthiophenol in 20 mL of toluene at 0 °C, and the solution was stirred overnight. The volatiles were removed under vacuum, leaving a white solid which was recrystallized from a mixture of toluene and pentane at −20 °C. Yield: 88%. ^1H NMR (C_6D_6, δ, ppm): 0.08, 0.10, 0.12, 0.20 (s, 6H, $Ga(CH_3)_2$), 2.55, 2.58, 2.61 (s, 6H, 2,6-$(C\mathbf{H}_3)_2C_6H_3$), 6.88 (s, 3H, 2,6-$(CH_3)_2C_6\mathbf{H}_3$). ^{13}C NMR (C_6D_6, δ, ppm): −1.9, −1.7, −0.7 ($Ga(CH_3)_2$), 24.2 (br, 2,6-$(\mathbf{C}H_3)_2C_6H_3$), 127.4, 127.5, 128.4, 128.6, 128.7, 142.5 (aryl).

X-ray Data Collection and Structure Refinement. Suitable crystals of compounds **1**−**9** were prepared using the procedures described in the Experimental Section. Crystals of each compound were inserted into thin-walled glass capillaries under an argon atmosphere in a drybox, which were plugged with grease, removed from the drybox, flame-sealed, and mounted on a goniometer head. Diffraction data were collected on a Syntex/Siemens $P2_1$ or R3 diffractometer using nickel-filtered Cu radiation (λ = 1.581 84 Å) or graphite-monochromatized MoK$\bar{\alpha}$ radiation (λ = 0.710 73 Å). The initial orientation matrices were obtained from 15 to 25 machine-centered reflections chosen from rotation photographs. Axial photographs were consistent with the crystal systems selected for all compounds. Ultimately, 25 high-angle reflections were used to determine the final cell constants and orientation matrices. The symmetries of the cells for **2**, **3**, **5**, **6**, **8**, and **9** were consistent with the space groups $P1$ and $P\bar{1}$. Successful refinement of the structures confirmed the space groups as $P\bar{1}$ for these six structures. Compounds **1**, **4**, and **7** were consistent with the monoclinic system and were assigned to the space groups $P2_1/c$ for **4** and **7** and $P2_1/n$ for **1**. In the cases of **1**, **2**, and **8**, absorption corrections were applied (ψ scans). Selected crystal and data collection parameters for all compounds are listed in Table 1.

For compounds **1**, **2**, and **4**−**9**, data reduction was carried out using the SHELXTL programs,[41] and data refinement was performed with SHELX-76.[42] For compound **3**, data reduction and solution were carried out using SHELXTL PC.[43] Scat-

---

(41) Sheldrick, G. M. *SHELXTL*; University of Göttingen: Göttingen, Federal Republic of Germany, 1978.

Table 1. Selected Experimental Parameters for the X-ray Diffraction Studies of [Mes$_2$Al(μ-SBz)]$_2$ (1), [Me$_2$Al(μ-SSiPh$_3$)]2 (2), [Mes$_2$Al(μ-SPh)]$_2$ (3), {Me$_2$Al[μ-S(2-*t*-BuC$_6$H$_4$)]}$_3$ (4), {Me$_2$Al[μ-S(2-Me$_3$Si)C$_6$H$_4$]}$_3$ (5), {Me$_2$Al[μ-S(2-*i*-PrC$_6$H$_4$)]}$_3$ (6), {*i*-Bu$_2$Al[μ-S(2,4,6-*i*-Pr$_3$C$_6$H$_2$)]}$_3$ (7), {Me$_2$Al[μ-S(2,6-Me$_2$C$_6$H$_3$)]}$_4$ (8), and {Me$_2$Ga[μ-S(2,6-Me$_2$C$_6$H$_3$)]}$_4$ (9)

cmpd	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
formula	$C_{25}H_{29}AlS$	$C_{40}H_{42}Al_2S_2Si_2$	$C_{24}H_{27}AlS$	$C_{36}H_{57}Al_3S_3$	$C_{33}H_{57}Al_3Si_3S_3$	$C_{33}H_{51}Al_3S_3$	$C_{69}H_{123}Al_3S_3$	$C_{20}H_{30}Al_2S_2$	$C_{20}H_{30}Ga_2S_2$
fw (amu)	388.55	697.03	374.52	666.98	715.20	624.90	1129.87	388.55	474.02
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No.2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a(Å)	10.660(4)	9.077(2)	11.068(5)	9.324(7)	10.149(4)	12.538(5)	13.935(2)	8.555(1)	8.525(2)
b(Å)	12.268(2)	13.847(3)	12.470(3)	18.632(5)	14.427(5)	13.180(2)	22.563(4)	11.869(1)	11.805(3)
c(Å)	17.793(3)	16.724(4)	17.654(5)	23.959(9)	15.159(4)	13.873(2)	25.044(4)	12.688(1)	12.714(4)
α (deg)		101.08(2)	90.97(2)		88.19(3)	74.38(1)		96.546(8)	96.36(2)
β (deg)	106.94(2)	95.34(2)	107.77(3)	98.31(5)	89.39(3)	64.18(2)	101.44(1)	106.34(1)	106.46(2)
γ (deg)		103.38(2)	112.23(3)		88.57(3)	69.44(2)		109.06(1)	108.90(2)
Z	4	2 (dimers)	4	4 (trimers)	2 (trimers)	2 (trimers)	4 (trimers)	2	2
volume (Å^3)	2226.0(9)	1986.0(7)	2143(2)	4119(4)	2218(1)	1913.7(9)	7718(2)	1137.9(3)	1131.6(6)
D_{calcd} (g/cm^3)	1.16	1.17	1.16	1.08	1.07	1.08	1.03	1.13	1.39
radiation type	Mo K$\bar{\alpha}^a$	Mo K$\bar{\alpha}^a$	Mo K$\bar{\alpha}^a$	Mo K$\bar{\alpha}^a$	Mo K$\bar{\alpha}^a$	Mo K$\bar{\alpha}^a$	Mo K$\bar{\alpha}^a$	Cu K$\bar{\alpha}^b$	Cu K$\bar{\alpha}^b$
temp (°C)	22	22	20	22	22	22	22	20	20
μ (cm^{-1})	1.82	2.25	1.97	2.33	3.17	2.49	1.35	27.5	47.67
R^c	0.067	0.0520	0.0593	0.0755	0.050	0.520	0.125	0.0495	0.0608
$R_w{}^d$	0.061	0.0514	0.0480	0.0517	0.050	0.0441	0.142	0.0522	0.0660

[a] Graphite monochormator, $\lambda = 0.710\ 73$ Å. [b] Nickel filter, $\lambda = 1.541\ 78$ Å. [c] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [d] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table 2. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of [Mes$_2$Al(μ-SBz)]$_2$ (1)

atom	x	y	z	U_{eq} (Å^2)^a
Al1	0.0124(2)	0.1050(2)	0.9404(1)	0.0421(8)
S1	−0.1307(2)	−0.0491(1)	0.9317(1)	0.0428(7)
C1	−0.2928(6)	−0.0032(5)	0.9398(4)	0.045(3)
C2	−0.3865(6)	−0.0987(5)	0.9252(4)	0.042(3)
C3	−0.4170(7)	−0.1569(6)	0.8555(4)	0.057(3)
C4	−0.5086(8)	−0.2400(6)	0.8432(5)	0.073(4)
C5	−0.5677(8)	−0.2683(6)	0.9001(7)	0.078(4)
C6	−0.5357(8)	−0.2104(7)	0.9699(5)	0.071(4)
C7	−0.4449(6)	−0.1253(6)	0.9828(4)	0.052(3)
C8	0.1358(6)	0.0962(6)	0.8758(3)	0.040(3)
C9	0.1999(6)	0.1928(5)	0.8640(4)	0.047(3)
C10	0.1811(8)	0.3010(6)	0.8995(5)	0.077(4)
C11	0.2899(7)	0.1904(6)	0.8193(4)	0.055(3)
C12	0.3172(6)	0.0954(7)	0.7860(4)	0.053(3)
C13	0.4132(7)	0.0941(6)	0.7383(4)	0.074(4)
C14	0.2572(6)	0.0001(6)	0.7995(4)	0.052(3)
C15	0.1690(6)	−0.0002(6)	0.8429(4)	0.044(3)
C16	0.1120(7)	−0.1091(5)	0.8563(4)	0.060(3)
C17	−0.1049(6)	0.2314(5)	0.9293(4)	0.044(3)
C18	−0.2060(8)	0.2389(6)	0.8576(5)	0.060(4)
C19	−0.2118(7)	0.1611(6)	0.7895(4)	0.070(4)
C20	−0.2993(8)	0.3206(7)	0.8448(6)	0.083(5)
C21	−0.2968(9)	0.3963(8)	0.9008(8)	0.101(6)
C22	−0.403(1)	0.4842(8)	0.8896(7)	0.146(7)
C23	−0.196(1)	0.3946(6)	0.9699(6)	0.080(5)
C24	−0.0974(7)	0.3148(6)	0.9854(5)	0.056(4)
C25	0.0140(9)	0.3266(5)	1.0578(5)	0.067(4)

[a] U_{eq} (Å^2) = $^1/_3\Sigma_i\Sigma_jU_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$.

tering factors[44] for neutral non-hydrogen atoms were used, and the data were corrected for Lorentz and polarization effects. Direct methods were used to obtain an initial solution for all of the structures and the positions for heavy atoms. The positions of the non-hydrogen atoms not found by the direct methods were located from successive difference Fourier map calculations. Full-matrix, least-squares refinement of positional and thermal parameters for non-hydrogen atoms was carried out by minimizing the function $\Sigma(w|F_o| - |F_c|)^2$ for all compounds except **3** and **4** which were refined using two- and three-blocked matrices, respectively. The hydrogen atoms were placed in calculated positions with a C−H bond distance of 0.96 Å, and their isotropic thermal parameters were fixed at 0.08 (**2**, **4**, **6**, **8**, and **9**), 0.10 (**1**), and 0.15 (**5**). All hydrogen atom positional parameters were allowed to ride with their parent carbon atoms during subsequent refinement.

In the final cycles of refinement all non-hydrogen atoms of **1**−**6**, **8**, and **9** were refined anisotropically. For compound **7**, only the Al and S atoms were refined anisotropically. The carbon atoms were refined isotropically, and the hydrogen atoms were not modeled because of the limited number of data. The structural solution of **7** was further complicated by disorder of one of the *i*-Pr and two of the *i*-Bu groups. The phenyl rings of **5** were refined as regular hexagons with C−C distances of 1.395 Å. The asymmetric unit for **1** is a Mes$_2$AlSBz moiety, the asymmetric unit for **2** is a complete dimeric molecule, and the asymmetric unit for **3** consists of two independent Mes$_2$AlSPh moieties. The asymmetric units of **4**−**7** are complete trimeric molecules, and the asymmetric units of **8** and **9** contain one-half of a tetrameric molecule. One and 14 reflections were omitted in the refinement of **5** and **7**, respectively, because of secondary extinction.

The residual electron densities are of no chemical significance (<0.5 electrons). Atomic coordinates and isotropic thermal parameters for the non-hydrogen atoms are presented in Tables 2−10. Selected bond distances and angles are listed in Tables 11 (**1**−**3**), 12 (**4**−**7**), and 13 (**8**, **9**). A complete listing of crystal and X-ray data collection parameters, bond distances and angles, anisotropic thermal parameters for the non-hydrogen atoms, and atomic coordinates and isotropic thermal parameters for the hydrogen atoms are deposited as supplementary material.

Results and Discussion

The aluminum and gallium thiolates prepared are colorless crystalline materials, sensitive to moisture and oxygen. All nine compounds have been characterized by single-crystal X-ray diffraction and form three separate classes of structures in the solid state: dimeric molecular units with four-membered (AlS)$_2$ rings, trimeric units with six-membered (AlS)$_3$ rings, and tetrameric units with eight-membered (AlS)$_4$ and (GaS)$_4$ rings.

Compounds **1**−**3**are dimeric in the solid state with planar or nearly planar four-membered (AlS)$_2$ rings.

---

(42) Sheldrick, G. M. *SHELX-76*; University Chemical Laboratory: Cambridge, England, 1976.

(43) *SHELXTL PC*; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1990.

(44) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4 (present distributor, D. Reidel, Dordrecht, The Netherlands).

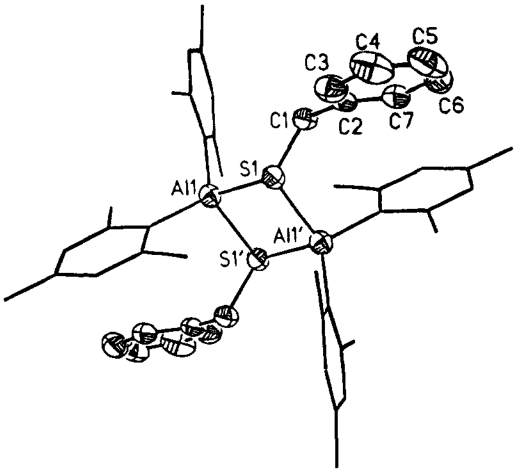


Figure 1. Diagram (50% thermal ellipsoids) of $[Mes_2Al(\mu\text{-}SBz)]_2$ (**1**) showing the atom-labeling scheme. The mesityl rings have been shown as wire frames, and the hydrogen atoms have been omitted for clarity.

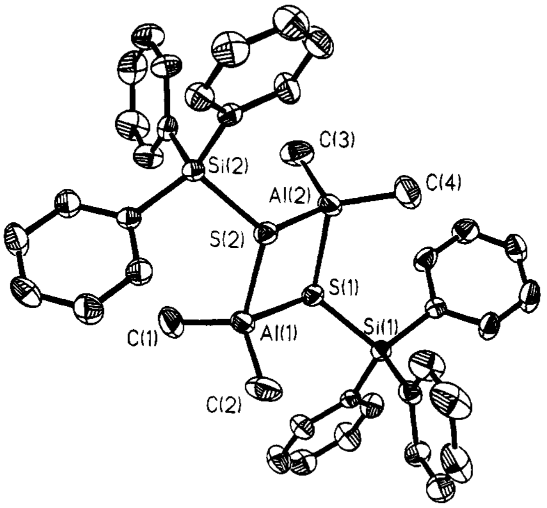


Figure 2. Diagram (20% thermal ellipsoids) of $[Me_2Al(\mu\text{-}SSiPh_3)]_2$ (**2**) showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity.

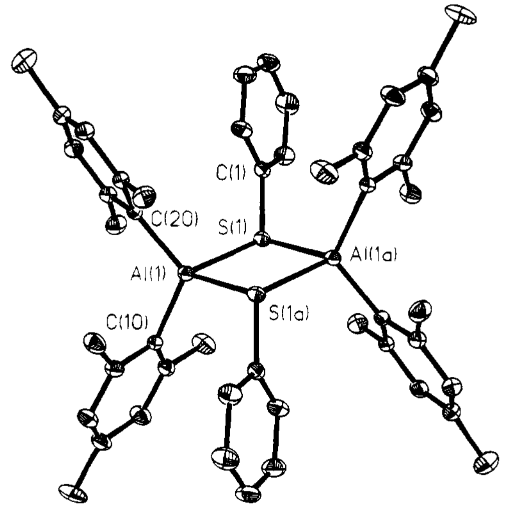


Figure 3. Diagram (20% thermal ellipsoids) of $[Mes_2Al(\mu\text{-}SPh)]_2$ (**3**) showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity.

ORTEP or thermal ellipsoid diagrams are given in Figures 1, 2, and 3. The average Al−C bond lengths are 1.977, 1.928, and 1.968 Å. Compounds **1** and **3**, with the longer bond lengths, are mesityl derivatives while **2** has methyl groups attached to the aluminum. The C−Al−C angles in **1**−**3** are in a narrow range between 118.7°−121.7°. Selected bond distances and angles are summarized in Table 11.

Table 3. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $[Me_2Al(\mu\text{-}SSiPh_3)]_2$ (2)

atom	x	y	z	U_{eq} (Å^2)[a]
S1	0.3175(2)	0.6140(1)	0.21865(8)	0.0472(5)
S2	0.1773(2)	0.3970(1)	0.26775(8)	0.0462(5)
Al1	0.3975(2)	0.4615(1)	0.2108(1)	0.0569(7)
Al2	0.0859(2)	0.5422(1)	0.2641(1)	0.0594(7)
Si1	0.4682(2)	0.7532(1)	0.29042(8)	0.0382(5)
Si2	0.0272(2)	0.2496(1)	0.20981(8)	0.0381(5)
C3	−0.0693(7)	0.5257(4)	0.1726(4)	0.092(3)
C4	0.0624(8)	0.6018(5)	0.3753(4)	0.114(4)
C1	0.3935(8)	0.4068(5)	0.0953(4)	0.102(3)
C2	0.5705(6)	0.4686(5)	0.2901(4)	0.091(3)
C11	0.3470(5)	0.8428(3)	0.3190(3)	0.040(2)
C12	0.2064(6)	0.8356(4)	0.2756(3)	0.063(2)
C13	0.1204(7)	0.9033(5)	0.2994(4)	0.076(3)
C14	0.1719(8)	0.9792(5)	0.3657(4)	0.072(3)
C15	0.3123(8)	0.9918(5)	0.4098(3)	0.082(3)
C16	0.3979(7)	0.9227(4)	0.3857(3)	0.064(3)
C17	0.5998(5)	0.7959(4)	0.2177(3)	0.040(2)
C18	0.6210(6)	0.8895(4)	0.1994(3)	0.057(2)
C19	0.7125(8)	0.9170(4)	0.1415(4)	0.075(3)
C20	0.7853(7)	0.8500(5)	0.1021(4)	0.073(3)
C21	0.7707(7)	0.7581(5)	0.1198(4)	0.071(3)
C22	0.6775(6)	0.7308(4)	0.1769(3)	0.057(2)
C23	0.5818(6)	0.7373(4)	0.3840(3)	0.050(2)
C24	0.5118(7)	0.6858(5)	0.4393(4)	0.087(3)
C25	0.600(1)	0.6754(7)	0.5082(4)	0.116(5)
C26	0.752(1)	0.7154(7)	0.5205(4)	0.107(5)
C27	0.8218(8)	0.7672(6)	0.4697(4)	0.093(4)
C28	0.7394(7)	0.7786(4)	0.4003(3)	0.066(3)
C29	−0.1027(6)	0.2508(4)	0.1170(3)	0.043(2)
C30	−0.2579(6)	0.2153(4)	0.1116(3)	0.061(2)
C31	−0.3556(6)	0.2162(5)	0.0423(4)	0.077(3)
C32	−0.2999(8)	0.2530(5)	−0.0196(4)	0.080(3)
C33	−0.1470(8)	0.2872(5)	−0.0168(4)	0.086(3)
C34	−0.0464(6)	0.2856(4)	0.0510(3)	0.065(2)
C35	−0.0892(5)	0.2161(4)	0.2915(3)	0.041(2)
C36	−0.1571(7)	0.2848(4)	0.3334(4)	0.064(3)
C37	−0.2452(8)	0.2605(5)	0.3946(4)	0.078(3)
C38	−0.2613(8)	0.1701(6)	0.4144(4)	0.082(3)
C39	−0.1961(8)	0.0998(5)	0.3738(4)	0.079(3)
C40	−0.1084(6)	0.1221(4)	0.3122(3)	0.056(2)
C41	0.1539(5)	0.1636(4)	0.1832(3)	0.041(2)
C42	0.2900(6)	0.1721(4)	0.2329(3)	0.056(2)
C43	0.3814(7)	0.1071(5)	0.2127(4)	0.070(3)
C44	0.3401(7)	0.0323(5)	0.1420(4)	0.071(3)
C45	0.2097(7)	0.0223(5)	0.0925(3)	0.073(3)
C46	0.1162(6)	0.0874(4)	0.1130(3)	0.060(2)

[a] U_{eq} (Å^2) $= \frac{1}{3}\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

The bridging groups in these three compounds are found in the *anti* conformation in the solid state. The sulfur atoms are pyramidal with the average value for the sum of the bond angles at the sulfur atom of **1**, **2**, and **3** being 306°, 330°, and 316°, respectively. The sum of these angles in $[Me_2Al(\mu\text{-}SMe)]_2$ is 306.7° in the gas phase[45] and 310.3° in the solid state.[31] In $[Me_2Al(\mu\text{-}SC_6F_5)]_2$,[14] this sum is 304.5°, and in the isostructural $[Me_2Ga(\mu\text{-}SC_6F_5)]_2$,[46] the sum of the angles around sulfur is 304.1°. In **1** and **3** the central $(AlS)_2$ ring is planar as required by symmetry, but in **2** the central ring deviates slightly from planarity with an angle of 7.2(2)° calculated between the Al(3)−S(1)−Al(4) and Al-

---

[45] Haaland, A.; Stokkeland, O.; Weidlein, J. *J. Organomet. Chem.* **1975**, *94*, 353.

[46] Hendershot, D. G.; Kumar, R.; Barber, M.; Oliver, J. P. *Organometallics* **1991**, *10*, 1917.

Chart 1

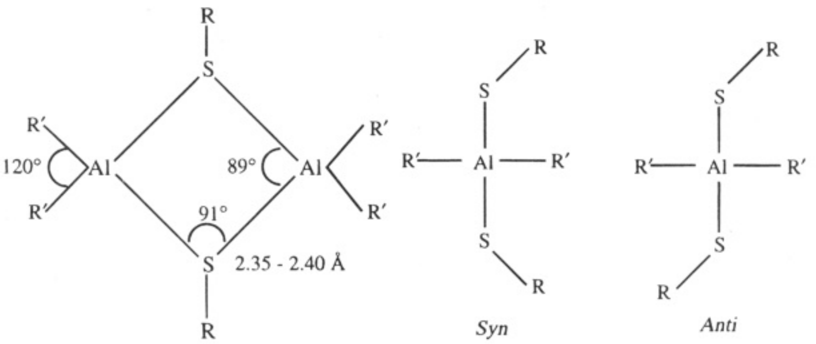
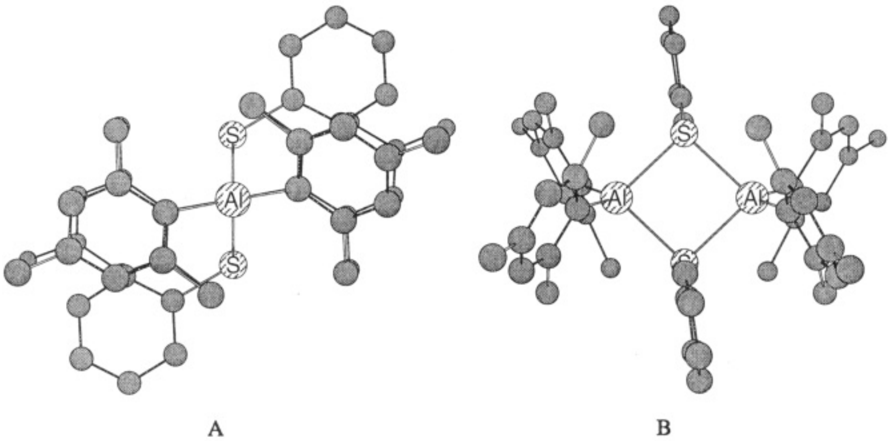


Chart 2. Views of 3 (A) along the Al−Al Vector and (B) Perpendicular to the $(AlS)_2$ Plane



(3)−S(2)−Al(4) planes. The butterfly conformation of **2** compares with that observed in $[Me_2Al(\mu\text{-}SC_6F_5)]_2$ (17.7°),[14] in $[I_2Ga(\mu\text{-S-}i\text{-Pr})]_2$ (36.7(2)°),[47] and in $[Me_2Ga(\mu\text{-}SC_6F_5)]_2$ (27.7°).[46] The structures of the cores of$[Ph_2Ga(\mu\text{-SEt})]_2$[16] and $[Me_2Al(\mu\text{-SMe})]_2$ in the gas phase[45] are planar. All of the compounds so far studied are found to have the groups attached to the sulfur atom in the *anti* conformation, but evidence gained from solution studies shows the energy difference between the *syn* and *anti* conformations is small.[19,35] Typical values for the structural parameters for the four-membered $(AlS)_2$ ring system along with projections showing the *syn* and *anti* conformations are shown in Chart 1.

Examination of the nonbonding distances in **1** and **3** shows that the shortest interaction in the mesitylaluminum derivatives is between the *ortho* methyl groups and the aluminum with ranges of 3.107−3.345 and 3.039−3.466 Å and average values of 3.272 and 3.260 Å, respectively. These short distances have minimal impact on the aggregation state but have often been involved in discussions on C−H bond activation.[48] The interactions of most importance to our arguments on aggregate formation and conformation stability are those occurring between the *ortho* methyl groups and those between these groups and the sulfur atom. Other interactions that may destabilize the aggregate or influence its conformation include those between the substituent on the sulfur and the aluminum, the interannular interactions, and those between the substituents on the aluminum atom. Many of these distances are within the range 3.4−4.0 Å and may contribute to the stability of the aggregate. Detailed calculations taking all of these interactions into account have not been made because of the large number of parameters and the unavailability of the force constants in these molecules. Chart 2, A and B, shows views of **3** along the Al−Al vector and perpendicular to the $(AlS)_2$ ring. The mesityl groups bound to aluminum and the phenyl groups bound to sulfur are oriented so that there are minimal steric interactions between them.

The conclusions that can be reached from these observations are that the central four-membered ring deviates little from planarity and that the orientation of the SR groups is normally found in the *anti* conformation in the solid state. The energy difference between the *anti* and the *syn* conformations is small, with both present in solution.[35] In the solid state, only the *anti* conformation has been reported and may be accounted for by small intermolecular interactions or crystal-packing forces.

Compounds **4**−**7** are the first trimeric organoaluminum thiolates that have been reported. The central $(AlS)_3$ rings in compounds **4**−**6** are in the chair conformation (Figures 4−6) with two of the substituents on the sulfur atoms oriented in an equatorial position and the other in an axial position. Compound **7** is in the skew-boat or twist conformation (Figure 7). Selected bond distances and bond angles for **4**−**7** are given in Table 12. The average Al−C bond distances in **4**−**7** are 1.94, 1.945, 1.934, and 1.96 Å. The first three of these are for methyl derivatives and are very close to the value observed for **2**. In **7**, the substituent is an isobutyl group. Examination of the axial and equatorial Al−C bond lengths (see Table 13) for **4**−**6** shows that the axial

---

[47] Hoffmann, G. G.; Burschka, C. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 970.

[48] Waggoner, K. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 3385.

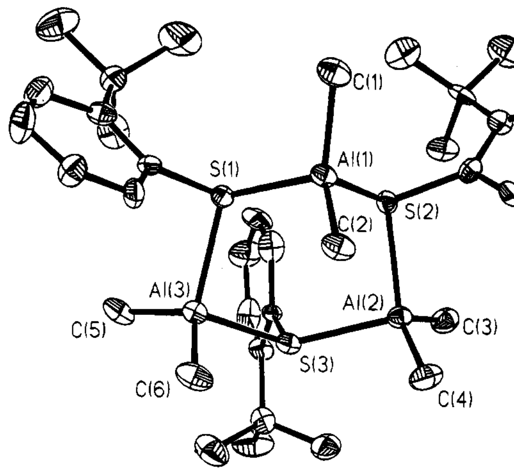


Figure 4. Diagram (20% thermal ellipsoids) of $\{Me_2Al[\mu\text{-}S(2\text{-}t\text{-}BuC_6H_4)]\}_3$ (**4**) showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity.

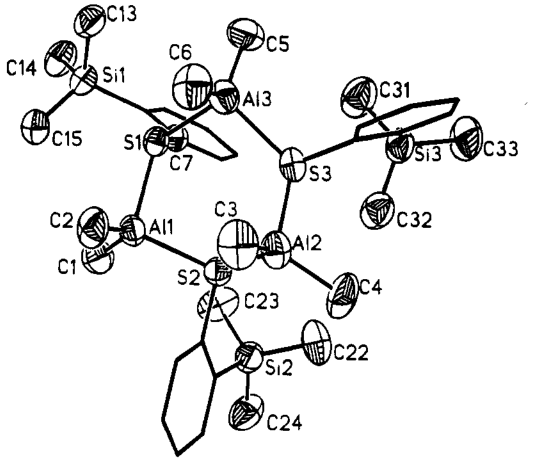


Figure 5. Diagram (50% thermal ellipsoids) of $\{Me_2Al[\mu\text{-}S(2\text{-}Me_3Si)C_6H_4]\}_3$ (**5**) showing the atom-labeling scheme. The aromatic rings have been shown as wire frames, and the hydrogen atoms have been omitted for clarity.

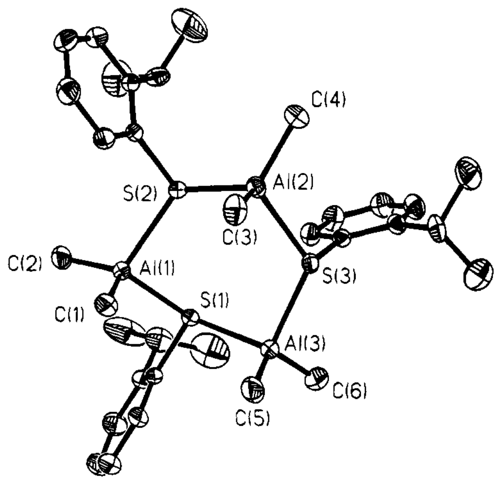


Figure 6. Diagram (20% thermal ellipsoids) of $\{Me_2Al[\mu\text{-}S(2\text{-}i\text{-}PrC_6H_4)]\}_3$ (**6**) showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity.

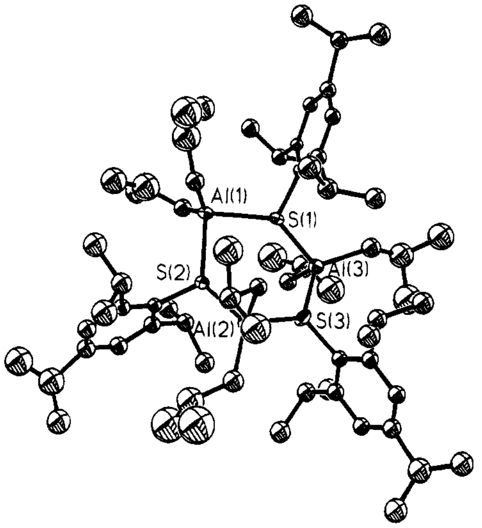


Figure 7. Diagram (5% thermal ellipsoids) of $\{i\text{-}Bu_2Al[\mu\text{-}S(2,4,6\text{-}i\text{-}Pr_3C_6H_2)]\}_3$ (**7**) showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity.

Al–C bond distances are all longer by approximately 0.02 Å than the equatorial Al–C distances, which suggests some differences in bond length as a function of orientation.

In **4–6**, the C–Al–C angles are between 118.3° and 123.2°, comparable to those observed in dimers, **1–3**. In **7**, these angles increase to 129°–130°, most probably as a result of the change of substituent on the metal from a methyl to an isobutyl group which also influences the ring conformation.

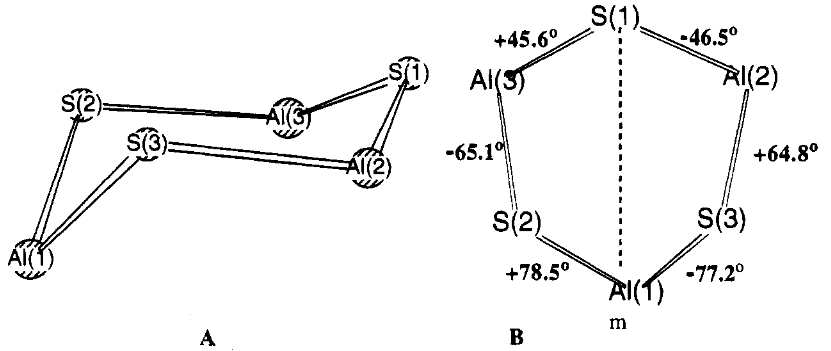
In **4–7**, there are fewer nonbonding distances shorter than 4.0 Å between groups on adjacent atoms in the ring than are observed in the dimers, suggesting that, with less steric crowding, trimers are favored. Increasing the bulk of the substituents on the metal by replacing the methyl groups with isobutyl groups and by adding isopropyl groups to the 2,6-positions on the aromatic rings attached to sulfur increases the number of nonbonding distances less than 4.0 Å, leading to added steric interactions and a change in the conformation of the ring. A comparison of the torsion angles in the two conformations and views of the ring structures are shown in Chart 3, A and B, and Chart 4, A and B.

This difference in ring conformation is seen in other ways. The sums of the angles around sulfur for compounds **4–6** are in the range 320°–338.5°. In compound **7**, the sum of the angles around sulfur is in the range 357°–360°; thus, the sulfur atoms in **7** are essentially planar. The sum of the angles around sulfur in the trimeric units is generally larger than in the dimers (304°–330°), showing that the sulfur atoms are approaching planarity. The changes in geometry appear to be associated with steric interactions and with angle strain in the ring system. In the trimeric oxygen-bridged compounds, the oxygen atom is planar or nearly planar in all cases, but additional O → Al π-interactions have been proposed that may account for this observation in these derivatives.[49] The implications of these differing geometries on reorganizational barriers will be discussed elsewhere.[35] A comparison of the endocyclic angles in **4–6** shows that the S–Al–S and Al–S–Al angles differ by about 10°, but the large angle around sulfur occurs at the apex while the corresponding angle around aluminum is the smallest in the ring, as shown in Chart 5. The greatest difference between **7** and **4–6** is observed at the sulfur atom where the angles around sulfur range from 127° to 132° in **7** and from 114° to

---

[49] Barron, A. R.; Dobbs, K. D.; Francl, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 39.

Chart 3. Chair Conformation of $\{Me_2Al[\mu\text{-}S(2\text{-}t\text{-}BuC_6H_4)]\}_3$ (4)[a]



[a] The six torsion angles are given adjacent to the central bond associated with the angle in **B**.

Table 4. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (×10³) for the Non-Hydrogen Atoms of $[Mes_2Al(\mu\text{-}SPh)]_2$ (3)

atom	*x*	*y*	*z*	U_{eq} (Å²)[a]
Al1	428(1)	−1208(1)	4927(1)	37(1)
S1	1589(1)	817(1)	5554(1)	39(1)
C1	2861(4)	1768(4)	5176(3)	38(2)
C2	3939(5)	2713(4)	5710(3)	56(3)
C3	4930(6)	3502(5)	5443(4)	79(3)
C4	4849(6)	3348(5)	4655(4)	76(4)
C5	3798(6)	2404(5)	4134(3)	66(3)
C6	2794(5)	1614(4)	4386(3)	53(3)
C10	89(5)	−2391(4)	5659(3)	37(2)
C11	621(5)	−2233(4)	6506(3)	48(3)
C12	273(6)	−3187(5)	6917(3)	62(3)
C13	−558(5)	−4311(4)	6527(3)	56(3)
C14	−1069(5)	−4471(4)	5698(3)	55(3)
C15	−767(5)	−3542(4)	5269(3)	44(2)
C16	1597(6)	−1044(4)	6996(3)	72(3)
C17	−932(6)	−5347(5)	6989(3)	90(4)
C18	−1371(5)	−3823(4)	4358(3)	61(3)
C20	1279(5)	−1401(3)	4140(3)	36(2)
C21	2632(5)	−1322(4)	4474(3)	45(3)
C22	3412(5)	−1350(4)	3998(4)	59(3)
C23	2892(7)	−1461(4)	3181(4)	61(3)
C24	1548(7)	−1579(4)	2829(3)	56(3)
C25	738(5)	−1564(4)	3287(3)	43(3)
C26	3293(5)	−1220(4)	5375(3)	63(3)
C27	3747(7)	−1460(5)	2654(4)	101(4)
C28	−733(6)	−1761(4)	2840(3)	62(3)
Al2	3762(2)	5181(1)	10337(1)	40(1)
S2	3941(1)	4734(1)	9061(1)	41(1)
C30	4026(5)	5901(4)	8476(3)	40(2)
C31	4871(5)	7064(4)	8797(3)	51(3)
C32	4952(6)	7918(4)	8301(3)	68(3)
C33	4204(7)	7623(5)	7502(3)	78(4)
C34	3344(7)	6490(5)	7191(3)	89(4)
C35	3243(6)	5613(4)	7670(3)	63(3)
C40	2641(5)	3857(4)	10760(3)	38(2)
C41	1776(5)	2707(4)	10364(3)	44(2)
C42	1259(5)	1821(4)	10792(3)	54(3)
C43	1536(5)	2023(4)	11612(3)	56(3)
C44	2307(5)	3161(5)	11996(3)	57(3)
C45	2874(5)	4064(4)	11590(3)	44(2)
C46	1333(6)	2374(4)	9469(3)	69(3)
C47	1011(7)	1049(5)	12064(3)	100(4)
C48	3780(6)	5271(4)	12086(3)	64(3)
C50	3523(5)	6664(4)	10316(3)	41(2)
C51	4459(5)	7795(4)	10740(3)	44(3)
C52	4143(5)	8760(4)	10593(3)	51(3)
C53	2899(6)	8658(4)	10052(3)	55(3)
C54	1949(5)	7564(5)	9655(3)	59(3)
C55	2238(5)	6587(4)	9775(3)	45(3)
C56	5826(5)	7983(4)	11363(3)	61(3)
C57	2577(6)	9730(5)	9898(4)	87(4)
C58	1146(5)	5413(5)	9300(3)	66(3)

[a] U_{eq} (Å²) = $^{1}/_{3}\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

123° in **4**−**6**. Again this shows the distorted configuration of **7**.

Table 5. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $\{Me_2Al[\mu\text{-}S(2\text{-}t\text{-}BuC_6H_4)]\}_3$ (4)

atom	*x*	*y*	*z*	U_{eq} (Å²)[a]
S1	0.1892(3)	0.1650(2)	0.2308(1)	0.046(1)
S2	0.2333(3)	0.2545(2)	0.3505(1)	0.048(1)
S3	0.1343(3)	0.0689(2)	0.3572(1)	0.047(1)
Al1	0.1009(4)	0.2743(2)	0.2601(2)	0.052(2)
Al2	0.1206(4)	0.1757(2)	0.4083(2)	0.051(2)
Al3	0.0716(4)	0.0618(2)	0.2593(2)	0.052(2)
C1	0.194(1)	0.3524(6)	0.2267(5)	0.074(6)
C2	−0.111(1)	0.2725(6)	0.2589(5)	0.066(6)
C3	0.245(1)	0.1673(7)	0.4792(5)	0.079(6)
C4	−0.087(1)	0.1936(6)	0.4046(5)	0.086(7)
C5	0.167(1)	−0.0204(6)	0.2321(5)	0.085(6)
C6	−0.138(1)	0.0668(6)	0.2463(5)	0.078(6)
C7	0.145(1)	0.1641(7)	0.1580(5)	0.049(5)
C8	0.242(1)	0.1575(7)	0.1185(6)	0.057(6)
C9	0.188(2)	0.1550(8)	0.0598(7)	0.082(8)
C10	0.039(2)	0.161(1)	0.0403(6)	0.098(8)
C11	−0.046(1)	0.1707(9)	0.0779(6)	0.067(6)
C12	−0.004(2)	0.1709(8)	0.1338(5)	0.063(6)
C13	0.407(2)	0.1533(9)	0.1370(6)	0.076(8)
C14	0.495(2)	0.146(1)	0.0868(7)	0.135(9)
C15	0.449(1)	0.0878(9)	0.1744(6)	0.093(7)
C16	0.464(1)	0.2211(9)	0.1678(8)	0.14(1)
C17	0.236(2)	0.3401(7)	0.3835(4)	0.052(6)
C18	0.369(1)	0.3773(8)	0.4052(6)	0.055(6)
C19	0.352(2)	0.4450(8)	0.4301(6)	0.072(7)
C20	0.221(2)	0.4748(7)	0.4309(6)	0.090(8)
C21	0.097(2)	0.4400(9)	0.4096(6)	0.077(7)
C22	0.104(2)	0.3737(8)	0.3875(5)	0.057(6)
C23	0.523(2)	0.3463(7)	0.4013(6)	0.060(6)
C24	0.642(1)	0.3953(8)	0.4319(6)	0.108(8)
C25	0.543(1)	0.2741(7)	0.4320(5)	0.076(7)
C26	0.545(1)	0.3395(8)	0.3392(6)	0.096(7)
C27	0.317(1)	0.0324(7)	0.3733(5)	0.044(6)
C28	0.353(2)	−0.0296(7)	0.4018(5)	0.058(6)
C29	0.502(2)	−0.0479(8)	0.4070(6)	0.083(8)
C30	0.599(2)	−0.005(1)	0.3819(8)	0.10(1)
C31	0.562(2)	0.0560(9)	0.3564(6)	0.085(8)
C32	0.416(2)	0.0767(8)	0.3509(5)	0.072(7)
C33	0.246(2)	−0.0774(8)	0.4273(6)	0.065(7)
C34	0.168(2)	−0.0355(7)	0.4696(6)	0.099(8)
C35	0.129(2)	−0.1064(7)	0.3805(7)	0.118(8)
C36	0.319(2)	−0.1412(8)	0.4594(7)	0.124(8)

[a] U_{eq} (Å²) = $^{1}/_{3}\sum_i\sum_j U_{ij}\, a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

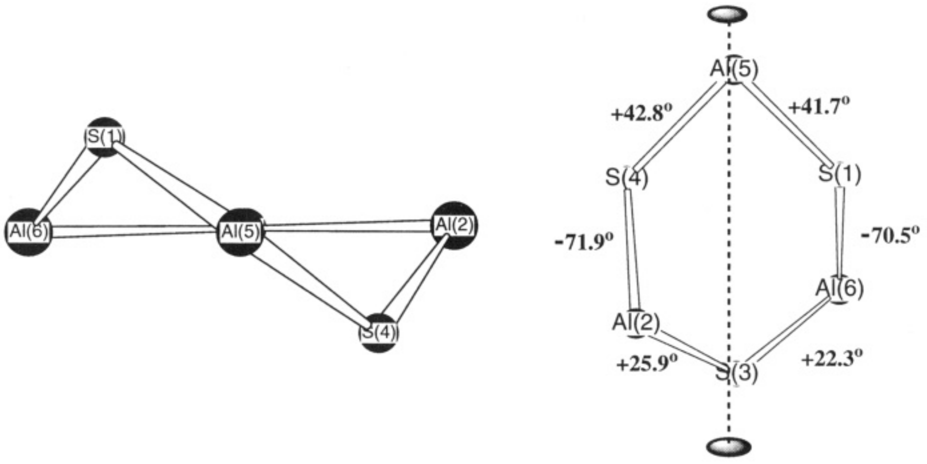
The trimeric structure is established with $[Me_2Al(\mu\text{-}OMe)]_3$ (gas phase),[21] $[Me_2Al(\mu\text{-}N(H)Me)]_3$,[25] $[H_2Al(\mu\text{-}NMe_2)]_3$,[26] and $[t\text{-}Bu_2Al(\mu\text{-}NH_2)]_3$[50] ring systems. Other Group 13 metals form six-membered rings such as $[Me_2In(\mu\text{-}AsMe_2)]_3$,[28] $[t\text{-}Bu_2Ga(\mu\text{-}OH)]_3$,[51] $[t\text{-}Bu_2Ga(\mu\text{-}NH_2)]_3$,[51]

---

(50) Interrante, L. V.; Sigel, G. A.; Garbauskas, M.; Hejna, C.; Slack, G. A. *Inorg. Chem.* **1989**, *28*, 252.

(51) Atwood, D. A.; Cowley, A. H.; Harris, P. R.; Jones, R. A.; Koschmieder, S. U.; Nunn, C. M.; Atwood, J. L.; Bott, S. G. *Organometallics* **1993**, *12*, 24.

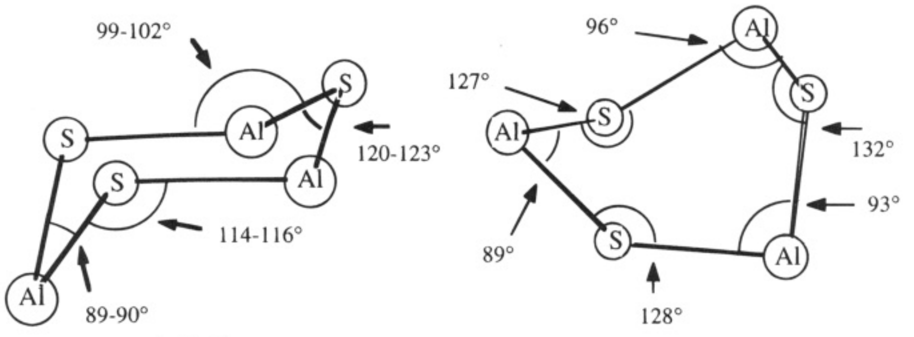
Chart 4. Twist-Boat Conformation of $\{i\text{-}Bu_2Al[\mu\text{-}S(2,4,6\text{-}i\text{-}Pr_3C_6H_2)]\}_3$ (7)[a]



A B

[a] The six torsion angles are given adjacent to the central bond associated with the angle in **B**.

Chart 5



4, 5, 6 **7**

$[(CH_2)_2NGaH_2]_3$,[27] and $\{Me_2Ga[\mu\text{-}P(Me)(Ph)]\}_3$.[24] Chair and skew-boat conformations have been observed for these derivatives with the primary difference in the structures related to the bridging chalcogen which is three-coordinate and the pnictinides which are four-coordinate.

Compounds **8** and **9** represent the first structurally-characterized cyclic tetrameric organoaluminum and -gallium thiolates. They are isomorphous and crystallize in an extended-chair conformation with alternating (2,6-dimethylphenyl)thiolato ligands bridging Me_2M moieties to form an eight-membered $(MS)_4$ ring with the Al or Ga atoms occupying the apical positions (Figures 8 and 9). Selected bond distances and angles are summarized in Table 13. The C−M−C bond angles show differences between the two independent metal atoms. In **8** these values are 126.0° and 120.3° while in **9** they are 129.5° and 124.2°. These values are in the range observed for $[Ph_2Ga(\mu\text{-}SEt)]_2$ (121.2°)[16] and for the aluminum derivative cited earlier. The average Al−C bond length in **8** is 1.943 Å, with equatorial bond lengths approximately 0.015 Å longer than the axial bond lengths. All of the Al−C bonds are in the range observed for organoaluminum compounds and compare favorably with the Al−C distances in other aluminum sulfur derivatives such as $[Me_2Al(\mu\text{-}SMe)]_2$ in the gas phase (1.945 Å),[45] $[Me_2Al(\mu\text{-}SMe)]_\infty$ in the solid state (1.945 Å),[31] and $[Me_2Al(\mu\text{-}SC_6F_5)]_2$ (1.942 Å average).[14] The Ga−C bond lengths in **9** (average 1.936 Å) are also comparable to those observed in other organogallium derivatives such as $[Me_2Ga(\mu\text{-}SC_6F_5)]_2$ (1.94 Å),[46] $[Ph_2Ga(\mu\text{-}SEt)]$ (1.964 Å),[16] and $[Me_2Ga(\mu\text{-}C{\equiv}CPh)]_2$ (1.952 Å).[52]

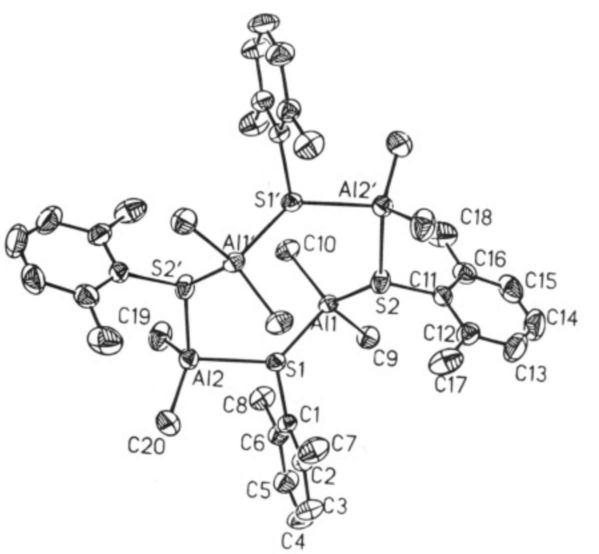


Figure 8. Diagram (50% thermal ellipsoids) of $\{Me_2Al[\mu\text{-}S(2,6\text{-}Me_2C_6H_3)]\}_4$ (**8**) showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity.

In both the aluminum and the gallium derivatives, the geometry around the sulfur atom is pyramidal with the sum of the angles around sulfur being 342.8° and

---

(52) Teclé, B.; Ilsley, W. H.; Oliver, J. P. *Inorg. Chem.* **1981**, *20*, 2335.

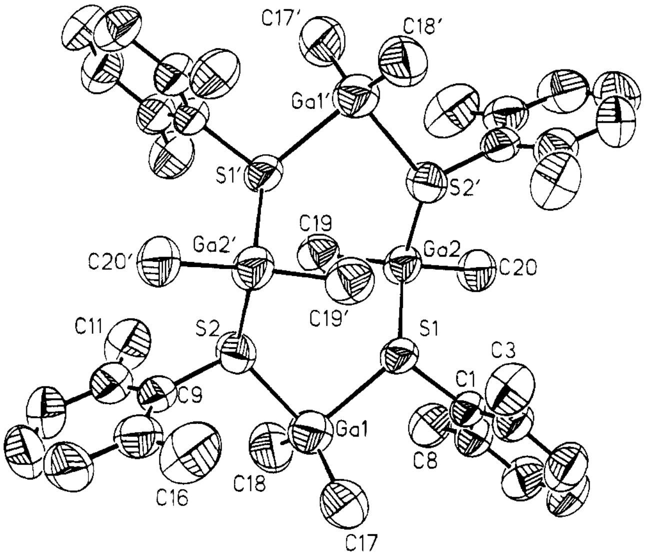


Figure 9. Diagram (50% thermal ellipsoids) of $\{Me_2Ga[\mu\text{-}S(2,6\text{-}Me_2C_6H_3)]\}_4$ (**9**) showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity.

Table 6. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $\{Me_2Al[\mu\text{-}S(2\text{-}SiMe_3)C_6H_4]\}_3$ (5)

atom	x	y	z	U_{eq} (Å^2)^a
S1	0.3266(1)	0.70685(9)	0.37788(9)	0.0498(5)
S2	0.2388(1)	0.73399(9)	0.14653(9)	0.0520(5)
S3	0.2915(1)	0.92511(9)	0.2570(1)	0.0586(6)
Al1	0.3389(2)	0.6250(1)	0.2462(1)	0.0563(7)
Al2	0.3644(2)	0.8680(1)	0.1196(1)	0.0647(7)
Al3	0.4034(2)	0.8603(1)	0.3814(1)	0.0627(7)
Si1	0.2394(2)	0.5814(1)	0.5605(1)	0.0588(6)
Si2	−0.0446(2)	0.6907(1)	0.0376(1)	0.0680(7)
Si3	0.0439(2)	1.0858(1)	0.2732(1)	0.0831(8)
C1	0.2239(6)	0.5196(4)	0.2525(4)	0.084(3)
C2	0.5295(5)	0.6060(4)	0.2315(4)	0.083(3)
C3	0.5542(5)	0.8433(4)	0.1120(4)	0.094(3)
C4	0.2817(6)	0.9421(4)	0.0258(4)	0.098(3)
C5	0.3313(6)	0.9152(4)	0.4866(4)	0.090(3)
C6	0.5937(5)	0.8482(4)	0.3647(4)	0.090(3)
C7	0.1601(3)	0.7090(2)	0.4144(2)	0.048(2)
C8	0.0680(3)	0.7637(2)	0.3675(2)	0.061(2)
C9	−0.0624(3)	0.7699(2)	0.3971(2)	0.074(3)
C10	−0.1008(3)	0.7212(2)	0.4738(2)	0.076(3)
C11	−0.0087(3)	0.6664(2)	0.5207(2)	0.065(2)
C12	0.1217(3)	0.6603(2)	0.4911(2)	0.050(2)
C13	0.3663(6)	0.6522(4)	0.6132(4)	0.080(3)
C14	0.1384(6)	0.5217(4)	0.6489(4)	0.084(3)
C15	0.3165(5)	0.4891(4)	0.4932(4)	0.071(2)
C16	0.2460(4)	0.6755(2)	0.0454(2)	0.054(2)
C17	0.3690(4)	0.6497(2)	0.0107(2)	0.070(3)
C18	0.3773(4)	0.6046(2)	−0.0693(2)	0.088(3)
C19	0.2628(4)	0.5852(2)	−0.1146(2)	0.093(3)
C20	0.1399(4)	0.6109(2)	−0.0799(2)	0.079(3)
C21	0.1315(4)	0.6560(2)	0.0001(2)	0.058(2)
C22	−0.0660(6)	0.8186(4)	0.0222(5)	0.100(3)
C23	−0.0817(6)	0.6518(5)	0.1530(4)	0.094(3)
C24	−0.1648(6)	0.6337(4)	−0.0348(4)	0.097(3)
C25	0.3268(5)	1.0452(2)	0.2483(3)	0.070(3)
C26	0.4570(5)	1.0714(2)	0.2348(3)	0.099(3)
C27	0.4868(5)	1.1651(2)	0.2263(3)	0.131(4)
C28	0.3864(5)	1.2327(2)	0.2313(3)	0.145(5)
C29	0.2562(5)	1.2064(2)	0.2448(3)	0.115(4)
C30	0.2264(5)	1.1127(2)	0.2533(3)	0.077(3)
C31	0.0227(7)	1.0380(5)	0.3874(4)	0.110(3)
C32	−0.0219(6)	1.0043(4)	0.1935(4)	0.092(3)
C33	−0.0560(8)	1.1959(5)	0.2612(5)	0.126(4)

[a] U_{eq} (Å^2) = $^1/_3\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

Chart 6. Comparison of Structural Parameters for $\{Me_2Al[\mu\text{-}S(2,6\text{-}Me_2C_6H_3)]\}_4$ (8), $\{Me_2Ga[\mu\text{-}S(2,6\text{-}Me_2C_6H_3)]\}_4$ (9), and $[Me_2Ga(\mu\text{-}OH)]_4$

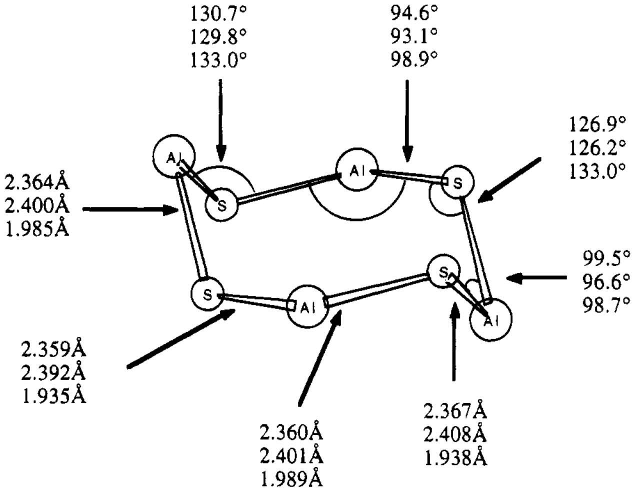
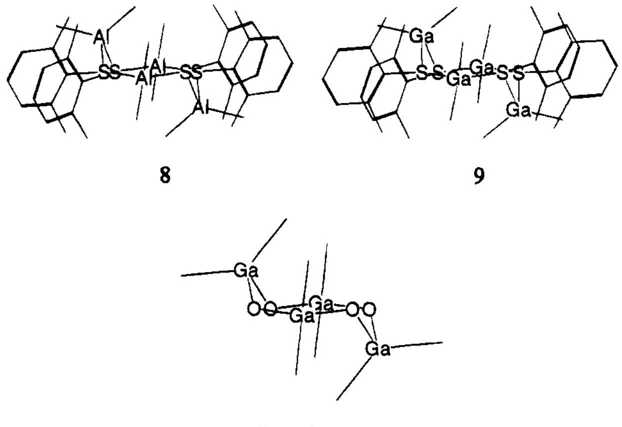


Chart 7



8 **9**

$[Me_2Ga(\mu\text{-}OH)]_4$

348.3° (**8**) and 340.7° and 346.0° (**9**). These values are intermediate with respect to the ideal values for planar and pyramidal geometries, suggesting that the chalcogen centers are slightly flattened. The endocyclic angles for **8** and **9** are listed in Table 13 and summarized in Chart 6, which shows the relationships between **8**, **9**, and the cyclic tetramer, $[Me_2Ga(\mu\text{-}OH)]_4$.[30] The similarities of the three tetrameric derivatives are illustrated in Chart 7, which shows the three molecules viewed along the plane containing the four chalcogen atoms. These angles are substantially larger than the Al−S−Al angles of **1** (90.89°), **2** (92.2° average), **3** (93.6° average), $[Me_2Al(\mu\text{-}SMe)]_2$ in the gas phase (94.5°),[45] $[Me_2Al(\mu\text{-}SC_6F_5)]_2$ (87.10°),[14] and the Ga−S−Ga angle of $[I_2Ga(\mu\text{-}S\text{-}i\text{-}Pr)]_2$ (84.7°)[47] and $[Ph_2Ga(\mu\text{-}SEt)]_2$ (86.42°).[16] They are also larger than those in **4**−**6** (summarized in Chart 5) but comparable to those in **7**.

In **8**, the C−Al−C angles are 120.3° and 126.0°. The corresponding angles in **9** are 124.2° and 129.5°. All other C−Al−C angles fall into the 115°−125° range typically observed for organoaluminum derivatives.[7,8] The C−M−C angles in **8** and **9** are at the top of this range, and this slight increase may be attributed to the high degree of flexibility of the eight-membered ring.

The Al−S and Ga−S bond lengths for all nine compounds are comparable to those observed in a number of aluminum and gallium thiolate bridged compounds as shown in Table 14. The Al−S bonds in thiolate bridges are longer than the distances observed

Table 7. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $\{Me_2Al[\mu\text{-}S(2\text{-}i\text{-}PrC_6H_4)]\}_3$ (6)

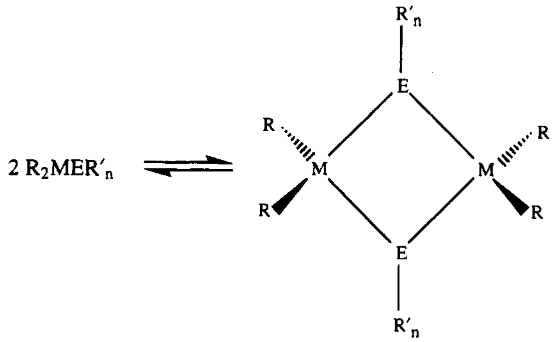
atom	x	y	z	U_{eq} (Å^2)[a]
S1	0.01457(9)	0.17500(8)	0.18960(8)	0.0524(5)
S2	0.17019(9)	0.31140(7)	0.22777(7)	0.0473(5)
S3	0.31928(9)	0.17467(8)	−0.01352(7)	0.0504(5)
Al1	0.0613(1)	0.17969(9)	0.33527(9)	0.0507(6)
Al2	0.3683(1)	0.2384(1)	0.10083(9)	0.0551(6)
Al3	0.1758(1)	0.0709(1)	0.0532(1)	0.0643(7)
C1	0.1588(4)	0.0389(3)	0.3788(3)	0.072(2)
C2	−0.0870(4)	0.2548(4)	0.4428(3)	0.078(2)
C3	0.4607(4)	0.1076(4)	0.1648(3)	0.080(3)
C4	0.4338(4)	0.3617(4)	0.0204(4)	0.087(3)
C5	0.2583(5)	−0.0705(4)	0.1115(4)	0.102(3)
C6	0.1172(5)	0.0898(5)	−0.0594(4)	0.107(4)
C7	−0.1050(4)	0.1047(3)	0.2557(3)	0.053(2)
C8	−0.2239(4)	0.1609(4)	0.2663(4)	0.068(3)
C9	−0.3134(4)	0.1015(5)	0.3204(4)	0.094(3)
C10	−0.2818(6)	−0.0054(6)	0.3601(4)	0.100(4)
C11	−0.1663(6)	−0.0597(4)	0.3488(4)	0.088(3)
C12	−0.0753(4)	−0.0048(4)	0.2966(3)	0.070(3)
C13	−0.2592(5)	0.2785(5)	0.2208(6)	0.104(4)
C14	−0.2461(8)	0.2904(6)	0.1068(9)	0.198(8)
C15	−0.3828(7)	0.3445(6)	0.2817(9)	0.217(7)
C16	0.2128(3)	0.3529(3)	0.3167(3)	0.048(2)
C17	0.1919(3)	0.4640(3)	0.3180(3)	0.054(2)
C18	0.2321(4)	0.4884(4)	0.3870(4)	0.073(3)
C19	0.2859(5)	0.4093(5)	0.4505(4)	0.087(3)
C20	0.3021(4)	0.3035(4)	0.4503(4)	0.079(3)
C21	0.2672(4)	0.2731(4)	0.3828(3)	0.065(2)
C22	0.1286(4)	0.5537(3)	0.2531(4)	0.073(3)
C23	0.0037(6)	0.6102(6)	0.3231(6)	0.147(5)
C24	0.1981(7)	0.6373(6)	0.1891(6)	0.165(5)
C25	0.2701(4)	0.2916(3)	−0.1020(3)	0.049(2)
C26	0.3496(4)	0.3122(3)	−0.2079(3)	0.056(2)
C27	0.3024(5)	0.4048(4)	−0.2705(4)	0.082(3)
C28	0.1837(5)	0.4699(4)	−0.2312(4)	0.086(3)
C29	0.1102(4)	0.4471(4)	−0.1296(4)	0.082(3)
C30	0.1509(4)	0.3594(3)	−0.0625(3)	0.069(2)
C31	0.4777(4)	0.2409(4)	−0.2565(3)	0.073(2)
C32	0.4879(5)	0.1789(5)	−0.3375(5)	0.115(4)
C33	0.5737(5)	0.3041(6)	−0.3064(5)	0.133(4)

[a] U_{eq} (Å^2) $= {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

for single Al−S bonds in the monomeric derivative, $Al[S(2,4,6\text{-}t\text{-}Bu_3C_6H_2)]_3$, (2.185 Å)[11] and in the bridging sulfido ligands of $I_4Al_4(\mu_3\text{-}S)_2(\mu_3\text{-}SR)_2$ (2.1 Å).[53] The Al−S distances involving the thiolate ligands of $I_4Al_4(\mu_3\text{-}S)_2(\mu_3\text{-}SR)_2$ (2.30 Å)[53] are only slightly shorter than those of **2**, **5**, and **8**. Other dimeric and trimeric aluminum thiolates display Al−S separations which are in good agreement with those reported here. For example, distances of 2.406, 2.338, 2.348, and 2.370 Å are found for $[Me_2Al(\mu\text{-}SC_6F_5)]_2$,[14] $[Me_2Al(2\text{-}SPy)]_2$,[54] $[Me_2Al(\mu\text{-}SMe)]_\infty$ (solid state),[31] and $[Me_2Al(\mu\text{-}SMe)]_2$ (gas phase),[45] respectively. The average Ga−S distance in **9** is 2.400 Å which is slightly longer than the analogous distances in $[I_2Ga(\mu\text{-}S\text{-}i\text{-}Pr)]_2$ (2.329 Å)[47] and $[Ph_2Ga(\mu\text{-}SEt)]_2$ (2.379 Å)[16] and significantly longer than the Ga−S distances in $[t\text{-}BuGa(\mu\text{-}S)Py]_3$ (2.242 Å)[23] and $[t\text{-}BuGa(\mu\text{-}S)]_4$ (2.359 Å).[34] Simple addition compounds, $(R_3Al\cdot SR_2)$, all have longer Al−S bonds which fall in the range 2.5−2.7 Å.[8]

A comparison of the endocyclic angles at the metal atom in the four-, six-, and eight-membered rings shows some increase around the metal center from 89° to 100°. These angles are similar to the S−M−S angles in four-membered ring systems such as $[I_2Ga(\mu\text{-}S\text{-}i\text{-}Pr)]_2$ (89.1°),[47] $[Me_2Al(\mu\text{-}SMe)]_2$ (gas phase) (85.5°),[45] $[Me_2Al(\mu\text{-}SC_6F_5)]_2$ (89.51°),[14] $[Ph_2Ga(\mu\text{-}SEt)]_2$ (93.58°),[16] and the six-membered ring of **5** (89.35−100.84°). In the linear polymer, $[Me_2Al(\mu\text{-}SMe)]_\infty$ (solid state),[31] an angle of 100.1° is found, suggesting that there is little strain at the metal atoms in the four-, six-, and eight-membered rings. The only other cyclic tetramers of this type reported are the $[Me_2Al(\mu\text{-}F)]_4$ molecule, which has bridging fluorine atoms,[29] and $[Me_2Ga(\mu\text{-}OH)]_4$.[30] The differences between the present systems and the $[Me_2Al(\mu\text{-}F)]_4$ derivative are in the description of the ring with the thiolate forming an "extended chair" and the fluoride a puckered ring. The center of inversion in the $[Me_2Ga(\mu\text{-}OH)]_4$ derivative gives similar features to the present systems. A comparison of the three chalcogen-bridged molecules is shown in Chart 7, all viewed parallel to the plane described by the four chalcogen atoms. The gross structural features are the same, but some differences occur as a result of the size of the bridging atoms and the changes in steric interactions. The internal angles in the rings differ substantially, and it appears that this results from the tendency of the oxygen to become planar when serving as a bridge between aluminum or gallium atoms.

Chart 8



The observation that diorganoaluminum thiolates form monomers, dimers, trimers, tetramers, and chains raises a number of questions concerning the factors which influence the aggregation states of these molecules in the solid state and in solution. In the present study, we can make some qualitative observations concerning these factors, but a more detailed discussion and the ability to predict aggregation states is still beyond our grasp. Coates[3] provided a brief comment on factors which may govern aggregation states nearly 30 years ago. The factors which he suggested are the "balance between entropy factors (favoring the formation of the maximum number of molecules, hence monomers or dimers) and steric factors." While this statement gives the broad overview of the problem, the difficulties are in assessing each of the interactions. The first distinction to be made is between monomers and dimers where the differences are the greatest since the monomer contains a single M−chalcogen (or pnictinide) bond while the dimer replaces this with a bridge of the form shown in Chart 8.

From the studies published, it is apparent that monomers result only when very bulky groups such as $2,4,6\text{-}t\text{-}Bu_3C_6H_2S$ are present on the metal center. This shows that the energy released in going from two single M−E bonds to two M−E−M bonds containing four M−E interactions in the bridge is sufficient to overcome the

---

[53] Boardman, A.; Small, R. W. H.; Worrall, I. J. *Inorg. Chim. Acta* **1986**, *120*, L23.

[54] Kumar, R.; de Mel, V. S. J.; Oliver, J. P. *Organometallics* **1989**, *8*, 2488.

Table 8. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $\{i\text{-Bu}_2\text{Al}[\mu\text{-S}(2,4,6\text{-}i\text{-Pr}_3\text{C}_6\text{H}_2)]\}_3$ (7)

atom	*x*	*y*	*z*	U_{eq} (Å^2)^a
S1	0.7562(4)	0.3076(3)	0.2018(3)	0.058(3)
S2	0.5338(5)	0.2896(3)	0.1263(3)	0.061(3)
S3	0.6906(5)	0.1664(3)	0.1557(3)	0.075(3)
Al1	0.6213(6)	0.3712(4)	0.1709(3)	0.062(3)
Al2	0.5278(5)	0.1929(4)	0.1613(3)	0.059(3)
Al3	0.8263(5)	0.2307(4)	0.1575(3)	0.058(3)
C1	0.820(2)	0.255(1)	0.083(1)	0.084(9)
C2	0.920(3)	0.276(2)	0.065(2)	0.16(2)
C3	0.969(4)	0.226(3)	0.050(2)	0.24(2)
C4	0.900(4)	0.325(3)	0.029(3)	0.27(3)
C5	0.941(2)	0.204(1)	0.212(1)	0.10(1)
C6	1.031(3)	0.177(2)	0.198(2)	0.17(2)
C7	1.106(3)	0.161(2)	0.250(2)	0.19(2)
C8	0.993(4)	0.118(3)	0.171(2)	0.24(2)
C9	0.646(2)	0.422(1)	0.111(1)	0.086(9)
C10	0.602(4)	0.482(3)	0.099(2)	0.22(2)
C11	0.634(3)	0.508(2)	0.047(2)	0.16(2)
C12	0.516(3)	0.503(2)	0.111(2)	0.18(2)
C13	0.569(2)	0.392(1)	0.237(1)	0.084(9)
C14	0.599(4)	0.450(2)	0.262(2)	0.20(2)
C15	0.688(3)	0.481(2)	0.270(1)	0.14(1)
C16	0.562(4)	0.451(2)	0.322(2)	0.22(2)
C17	0.526(2)	0.204(1)	0.240(1)	0.069(8)
C18	0.421(2)	0.200(1)	0.254(1)	0.10(1)
C19	0.429(3)	0.240(2)	0.310(2)	0.18(2)
C20	0.405(3)	0.139(2)	0.274(2)	0.19(2)
C21	0.455(2)	0.140(1)	0.109(1)	0.11(1)
C22	0.338(4)	0.147(2)	0.091(2)	0.18(2)
C23	0.307(5)	0.149(3)	0.031(3)	0.29(3)
C24	0.292(5)	0.106(3)	0.112(3)	0.31(4)
C30	0.839(1)	0.3409(6)	0.2590(6)	0.049(7)
C31	0.898(1)	0.3881(6)	0.2501(6)	0.042(6)
C32	0.952(1)	0.4189(6)	0.2943(6)	0.056(7)
C33	0.947(1)	0.4025(6)	0.3473(6)	0.066(8)
C34	0.887(1)	0.3553(6)	0.3562(6)	0.063(8)
C35	0.833(1)	0.3245(6)	0.3120(6)	0.066(8)
C36	0.773(2)	0.267(1)	0.325(1)	0.10(1)
C37	0.845(2)	0.217(1)	0.347(1)	0.10(1)
C38	0.706(2)	0.287(2)	0.365(1)	0.12(1)
C39	1.003(2)	0.444(1)	0.396(1)	0.077(9)
C40	0.925(2)	0.490(1)	0.410(1)	0.11(1)
C41	1.041(2)	0.403(1)	0.446(1)	0.11(1)
C42	0.909(2)	0.407(1)	0.193(1)	0.075(9)
C43	1.013(2)	0.387(1)	0.182(1)	0.09(1)
C44	0.903(2)	0.476(1)	0.183(1)	0.09(1)
C50	0.436(1)	0.3078(7)	0.0704(6)	0.051(7)
C51	0.343(1)	0.3205(7)	0.0792(6)	0.072(8)
C52	0.265(1)	0.3278(7)	0.0349(6)	0.086(9)
C53	0.282(1)	0.3223(7)	−0.0181(6)	0.088(9)
C54	0.375(1)	0.3096(7)	−0.0268(6)	0.085(9)
C55	0.453(1)	0.3023(7)	0.0174(6)	0.077(9)
C56	0.557(2)	0.290(1)	0.004(1)	0.085(9)
C57	0.583(2)	0.338(1)	−0.037(1)	0.11(1)
C58	0.558(2)	0.227(1)	−0.019(1)	0.11(1)
C59	0.149(4)	0.370(2)	−0.078(2)	0.21(2)
C60	0.196(3)	0.320(3)	−0.078(2)	0.19(2)
C61	0.152(3)	0.260(2)	−0.080(2)	0.15(1)
C62	0.320(2)	0.329(1)	0.139(1)	0.10(1)
C63	0.227(3)	0.295(2)	0.144(2)	0.16(1)
C64	0.313(3)	0.395(2)	0.148(1)	0.14(1)
C70	0.711(1)	0.0876(5)	0.1520(8)	0.061(8)
C71	0.726(1)	0.0530(5)	0.1991(8)	0.069(8)
C72	0.733(1)	−0.0084(5)	0.1954(8)	0.072(8)
C73	0.726(1)	−0.0353(5)	0.1446(8)	0.085(9)
C74	0.711(1)	−0.0008(5)	0.0975(8)	0.072(8)
C75	0.703(1)	0.0607(5)	0.1012(8)	0.074(8)
C76	0.693(2)	0.095(1)	0.048(1)	0.090(9)
C77	0.601(2)	0.072(1)	0.006(1)	0.11(1)
C78	0.789(2)	0.090(2)	0.024(1)	0.12(1)
C79	0.731(3)	−0.104(2)	0.137(2)	0.14(1)
C80	0.632(3)	−0.130(2)	0.110(1)	0.13(1)
C81	0.785(2)	−0.135(2)	0.186(1)	0.13(1)
C82	0.738(2)	0.083(1)	0.259(1)	0.09(1)
C83	0.837(2)	0.065(1)	0.294(1)	0.11(1)
C84	0.651(2)	0.060(2)	0.283(1)	0.12(1)

^{a} U_{eq} (Å^2) = $^1/_3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

Table 9. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $\{\text{Me}_2\text{Al}[\mu\text{-S}(2,6\text{-Me}_2\text{C}_6\text{H}_3)]\}_4$ (8)

atom	*x*	*y*	*z*	U_{eq} (Å^2)^a
S1	0.0230(1)	0.41374(9)	0.66207(8)	0.0475(4)
S2	0.0992(2)	0.7206(1)	0.62097(8)	0.0577(5)
Al1	0.2595(1)	0.5988(1)	0.68751(9)	0.0441(5)
Al2	−0.0351(2)	0.2207(1)	0.5528(1)	0.0543(6)
C1	0.0027(5)	0.3807(3)	0.7932(3)	0.047(2)
C2	−0.1510(5)	0.3765(4)	0.8146(3)	0.056(2)
C3	−0.1714(7)	0.3456(5)	0.9125(4)	0.080(3)
C4	−0.0443(8)	0.3207(5)	0.9886(4)	0.085(3)
C5	0.1052(7)	0.3253(4)	0.9672(4)	0.073(3)
C6	0.1333(5)	0.3547(4)	0.8700(3)	0.056(2)
C7	−0.2941(6)	0.4033(5)	0.7331(4)	0.082(3)
C8	0.3003(6)	0.3561(5)	0.8506(4)	0.072(2)
C9	0.3807(6)	0.6696(4)	0.8490(3)	0.066(2)
C10	0.3671(5)	0.5621(4)	0.5789(4)	0.065(2)
C11	0.1548(5)	0.8510(4)	0.7297(3)	0.051(2)
C12	0.0207(6)	0.8582(4)	0.7709(4)	0.065(2)
C13	0.064(1)	0.9550(6)	0.8596(5)	0.093(3)
C14	0.229(1)	1.0400(6)	0.9056(5)	0.105(4)
C15	0.3581(8)	1.0352(5)	0.8654(5)	0.090(3)
C16	0.3243(6)	0.9401(4)	0.7749(4)	0.067(2)
C17	−0.1629(7)	0.7665(6)	0.7245(5)	0.101(3)
C18	0.4674(7)	0.9374(6)	0.7305(5)	0.104(3)
C19	0.1673(7)	0.1765(5)	0.5625(4)	0.087(3)
C20	−0.2347(7)	0.1131(4)	0.5816(5)	0.095(3)

^{a} U_{eq} (Å^2) = $^1/_3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

steric and entropy factors in all but the most hindered molecules. The differences between the dimers and higher aggregates are not so readily assessed since the number of bonds remains constant. This is represented in Chart 9.

In these systems the balance is between entropy and the variety of steric interactions possible. It is not likely that any significant contribution from changes in bond energy occurs since the number and type of bonds remain constant. The steric interactions include the repulsion between groups on the same atom, the repulsion between those on adjacent atoms, cross-ring or chain interactions such as 1−3 diaxial interactions, and the various kinds of ring strain that may occur. As pointed out by many authors, the interaction between groups on adjacent atoms should increase as the ring size expands; at the same time, cross-ring interactions should diminish and the flexibility of the ring may decrease any ring strain present. To account for all of this stretching and bending, force constants are needed for all bonds. Barron has studied a number of $[\text{R}_2\text{Al}(\mu\text{-OR}')]_n$ derivatives which contain four- and six-membered rings by NMR spectroscopy and has carried out a few calculations designed to provide information about the stability of these rings and their conformations.[55] He has shown that increasing chain length of the R′ group favors dimers but has noted that it is

---

(55) Rogers, J. H.; Apblett, A. W.; Cleaver, W. M.; Tyler, A. N.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1992**, 3179.

(56) Fernholt, L.; Haaland, A.; Hargittai, M.; Seip, R.; Weidlein, J. *Acta Chem. Scand.* **1981**, *A35*, 529.

(57) Boardman, A.; Jeffs, S. E.; Small, R. W. H.; Worrall, I. J. *Inorg. Chim. Acta* **1985**, *99*, L39.

Chart 9

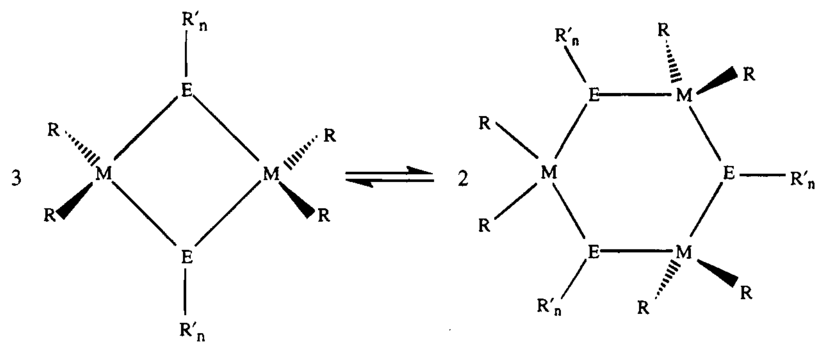


Table 10. Atomic Coordinates and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $\{Me_2Ga[\mu\text{-}S(2,6\text{-}Me_2C_6H_3)]\}_4$ (9)

atom	*x*	*y*	*z*	U_{eq} (Å^2)[a]
Ga1	−0.0356(2)	0.2161(1)	0.5541(1)	0.0936(7)
Ga2	0.2655(2)	0.5994(1)	0.68897(8)	0.0724(5)
S1	0.0201(3)	0.4133(2)	0.6614(2)	0.068(1)
S2	−0.0949(3)	0.2799(2)	0.3789(2)	0.078(1)
C1	0.001(1)	0.3797(7)	0.7935(6)	0.063(4)
C2	−0.149(1)	0.3774(8)	0.8151(7)	0.075(4)
C3	−0.297(1)	0.405(1)	0.7347(9)	0.098(6)
C4	−0.169(1)	0.346(1)	0.9158(9)	0.093(6)
C5	−0.042(2)	0.321(1)	0.9886(8)	0.099(6)
C6	0.104(2)	0.324(1)	0.9661(8)	0.090(6)
C7	0.133(1)	0.3544(8)	0.8693(7)	0.074(4)
C8	0.297(1)	0.356(1)	0.8498(8)	0.090(5)
C9	−0.153(1)	0.1506(8)	0.2706(7)	0.069(4)
C10	−0.021(2)	0.1419(9)	0.2286(8)	0.087(5)
C11	0.165(2)	0.231(1)	0.275(1)	0.117(7)
C12	−0.064(2)	0.044(1)	0.138(1)	0.106(7)
C13	−0.229(3)	−0.040(1)	0.092(1)	0.125(9)
C14	−0.362(2)	−0.035(1)	0.133(1)	0.111(6)
C15	−0.322(1)	0.0621(9)	0.2242(8)	0.085(5)
C16	−0.465(2)	0.068(1)	0.268(1)	0.128(7)
C17	−0.239(2)	0.114(1)	0.5815(9)	0.120(6)
C18	0.168(2)	0.175(1)	0.5638(9)	0.107(6)
C19	0.368(1)	0.5632(9)	0.5767(8)	0.080(5)
C20	0.381(1)	0.6714(9)	0.8513(7)	0.086(5)

[a] U_{eq} (Å^2) = $\frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

difficult to make quantitative predictions for these systems. Alternatively, *ab initio* calculations describing the system could be carried out. At the present time, a number of the necessary force constants are unavailable, and an *ab initio* calculation is beyond the scope of this work.

We have, however, looked at several of these parameters in which the major differences arise from substituent interactions and compared these with compounds reported in the literature to obtain a qualitative understanding of the critical factors governing these equilibria. The only monomer reported for an aluminum thiolate is $Al(SMes^*)_3$.[11] The shortest nonbonding interactions, in the range of 2.5−2.8 Å, are between hydrogen atoms on the *tert*-butyl groups and the metal atom. The separations between *tert*-butyl groups on adjacent rings are in the range 3.73−3.83 Å. The *tert*-butyl groups effectively form a cage around the aluminum center, preventing dimerization.

In the typical dimeric compounds the closest nonbonding interactions that are likely to influence the state of aggregation substantially are those between the groups bound to aluminum and the groups on sulfur and interactions which occur across the ring. The groups bound to sulfur are normally separated by large distances because of their orientation in the *trans* configuration in the dimers or in equatorial positions on the larger rings. In the trimeric molecules, the rings become more flexible, in many cases undergoing inversion with relatively low energy barriers.[35] In the solid state, the rings are found in chair and skew-boat conformation, and the closest nonbonding interactions

Table 11. Selected Bond Distances (Å) and Angles (deg) for $[Mes_2Al(\mu\text{-}SBz)]_2$ (1), $[Me_2Al(\mu\text{-}SSiPh_3)]_2$ (2), and $[Mes_2Al(\mu\text{-}SPh)]_2$ (3)

$[Mes_2Al(\mu\text{-}SBz)]_2$ (**1**)		$[Me_2Al(\mu\text{-}SSiPh_3)]_2$ (**2**)		$[Mes_2Al(\mu\text{-}SPh)]_2$ (**3**)	
		Bond Distances			
Al1−S1	2.405(3)	Al1−S1	2.372(2)	Al1−S1	2.416(2)
Al1′−S1	2.358(2)	Al2−S1	2.368(2)	Al1′−S1	2.371(2)
		Al1−S2	2.358(2)	Al2−S2	2.395(2)
		Al2−S2	2.355(2)	Al2′−S2	2.398(2)
Al1−C17	1.966(7)	Al2−C4	1.936(5)	Al1−C20	1.958(6)
Al1−C8	1.987(5)	Al2−C3	1.921(6)	Al1−C10	1.982(5)
		Al1−C2	1.930(6)	Al2−C40	1.969(5)
		Al1−C1	1.927(5)	Al2−C50	1.964(6)
S1−C1	1.863(6)	S1−Si1	2.147(2)	S1−C1	1.781(5)
		S2−Si2	2.160(2)	S2−C30	1.789(5)
		Bond Angles			
S1−Al1−S1′	89.11(8)	S1−Al1−S2	87.51(6)	S1−Al1−S1′	85.6(1)
		S1−Al2−S2	87.68(6)	S2−Al2−S2′	87.2(1)
Al1−S1−Al1′	90.89(8)	Al1−S1−Al2	91.85(6)	Al1−S1−Al1′	94.4(1)
		Al1−S2−Al2	92.54(6)	Al2−S2−Al2′	92.8(1)
C8−Al1−C17	119.6(3)	C3−Al2−C4	121.4(3)	C10−Al1−C20	118.7(2)
		C1−Al1−C2	120.7(3)	C40−Al2−C50	121.7(3)
Al1−S1−C1	110.0(2)	Al1−S1−Si1	118.35(7)	Al1−S1−C1	116.8(2)
Al1′−S1−C1	105.1(2)	Al2−S1−Si1	91.85(6)	Al1′−S1−C1	108.3(2)
		Al2−S2−Si2	118.21(7)	Al2−S2−C30	112.2(2)
		Al1−S2−Si2	119.97(6)	Al2′−S2−C30	108.5(2)

Table 12. Selected Bond Distances (Å) and Angles (deg) for {Me$_2$Al[μ-S(2-*t*-BuC$_6$H$_4$)]}$_3$ (4), {Me$_2$Al[μ-S(2-SiMe$_3$)C$_6$H$_4$]}$_3$ (5), {Me$_2$Al[μ-S(2-*i*-PrC$_6$H$_4$)]}$_3$ (6), and {*i*-Bu$_2$Al[μ-S(2,4,6-*i*-Pr$_3$C$_6$H$_2$)]}$_3$ (7)

4		5		6		7	
			Bond Distances				
Al1−S1	2.340(5)	Al1−S1	2.351(2)	Al1−S1	2.357(3)	Al1−S1	2.37(1)
Al3−S1	2.363(5)	Al3−S1	2.368(2)	Al3−S1	2.380(2)	Al3−S1	2.37(1)
Al1−S2	2.363(4)	Al1−S2	2.365(2)	Al1−S2	2.366(2)	Al1−S2	2.36(1)
Al2−S2	2.367(5)	Al2−S2	2.365(2)	Al2−S2	2.371(2)	Al2−S2	2.36(1)
Al2−S3	2.349(5)	Al2−S3	2.369(2)	Al2−S3	2.352(3)	Al2−S3	2.38(1)
Al3−S3	2.336(4)	Al3−S3	2.366(2)	Al3−S3	2.358(2)	Al3−S3	2.38(1)
Al3−C6 (a)	1.93(1)	Al3−C6 (a)	1.949(6)	Al3−C6 (e)	1.92(1)	Al3−C1	1.94(3)
Al3−C5 (e)	1.93(1)	Al3−C5 (e)	1.932(7)	Al3−C5 (a)	1.939(7)	Al3−C5	1.98(3)
Al2−C4 (a)	1.95(1)	Al2−C4 (e)	1.937(7)	Al2−C4 (e)	1.930(6)	Al2−C17	1.99(2)
Al2−C3 (e)	1.92(1)	Al2−C3 (a)	1.953(6)	Al2−C3 (a)	1.942(6)	Al2−C21	1.91(3)
Al1−C2 (a)	1.97(1)	Al1−C2 (a)	1.958(6)	Al1−C2 (e)	1.936(6)	Al1−C13	1.99(2)
Al−C1 (e)	1.92(1)	Al1−C1 (e)	1.940(6)	Al1−C1 (a)	1.936(6)	Al1−C9	1.95(3)
			Bond Angles				
S1−Al1−S2	88.8(2)	S1−Al1−S2	100.84(8)	S1−Al1−S2	90.22(8)	S1−Al1−S2	89.1(3)
S1−Al3−S3	100.6(2)	S1−Al3−S3	99.20(8)	S1−Al3−S3	99.89(8)	S1−Al3−S3	93.2(3)
S2−Al2−S3	99.1(2)	S2−Al2−S3	89.35(8)	S2−Al2−S3	101.52(7)	S2−Al2−S3	96.1(3)
Al1−S1−Al3	115.0(2)	Al1−S1−Al3	120.13(8)	Al1−S1−Al3	115.83(7)	Al1−S1−Al3	131.5(3)
Al1−S1−C7	105.5(5)	Al1−S1−C7	108.0(1)	Al1−S1−C7	101.9(2)	Al1−S1−C30	110.2(6)
Al3−S1−C7	103.3(5)	Al3−S1−C7	107.6(1)	Al3−S1−C7	106.9(2)	Al3−S1−C30	114.6(6)
Al1−S2−Al2	114.6(2)	Al1−S2−Al2	113.53(8)	Al1−S2−Al2	114.24(7)	Al1−S2−Al2	126.8(3)
Al1−S2−C17	103.9(4)	Al1−S2−C16	102.7(1)	Al2−S2−C16	99.8(1)	Al2−S2−C50	115.2(6)
Al2−S2−C17	106.1(4)	Al2−S2−C16	104.4(1)	Al1−S2−C16	105.9(2)	Al1−S2−C50	115.4(6)
Al2−S3−Al3	123.2(2)	Al2−S3−Al3	114.85(8)	Al2−S3−Al3	122.5(1)	Al2−S3−Al3	127.6(4)
Al2−S3−C27	108.9(4)	Al2−S3−C25	103.5(2)	Al2−S3−C25	107.3(2)	Al2−S3−C70	114.3(6)
Al3−S3−C27	106.4(4)	Al3−S3−C25	108.1(2)	Al3−S3−C25	107.3(2)	Al3−S3−C70	118.1(6)
C1−Al1−C2	121.1(5)	C1−Al1−C2	120.2(3)	C1−Al1−C2	119.6(3)	C9−Al1−C13	130(1)
C3−Al2−C4	121.5(5)	C3−Al2−C4	118.3(3)	C3−Al2−C4	122.6(2)	C17−Al2−C21	130(1)
C5−Al3−C6	119.3(5)	C5−Al3−C6	120.2(3)	C5−Al3−C6	123.2(3)	C1−Al3−C5	129(1)

Table 13. Selected Bond Distances (Å) and Angles (deg) for {Me$_2$Al[μ-S(2,6-Me$_2$C$_6$H$_3$)]}$_4$ (8) and {Me$_2$Ga[μ-S(2,6-Me$_2$C$_6$H$_3$)]}$_4$ (9)

8		9	
	Bond Distances		
Al1−S1	2.364(1)	Ga1−S1	2.392(2)
Al2−S1	2.359(1)	Ga1−S2	2.401(1)
Al1−S2	2.367(1)	Ga2−S1	2.400(2)
Al2′−S2	2.360(1)	Ga2−S2′	2.408(2)
Al1−C9	1.955(3) (e)	Ga1−C17 (e)	1.91(1)
Al1−C10	1.944(3) (a)	Ga1−C18 (a)	1.92(1)
Al2−C19	1.944(5) (e)	Ga2−C20 (e)	1.967(6)
Al2−C20	1.927(5) (a)	Ga2−C19 (a)	1.946(6)
S1−C1	1.794(2)	S1−C1	1.768(5)
S2−C11	1.785(3)	S2−C9	1.807(4)
	Bond Angles		
Al1−S1−Al2	126.92(5)	Ga1−S1−Ga2	126.21(8)
Al1−S2−Al2′	130.68(4)	Ga2′−S2−Ga1	129.77(7)
S1−Al1−S2	99.46(5)	S1−Ga1−S2	93.07(5)
S1−Al2−S2′	94.60(4)	S1−Ga2−S2′	96.6(5)
C9−Al1−C10	126.0(2)	C19−Ga2−C20	129.5(4)
C19−Al2−C20	120.3(2)	C17−Ga1−C18	124.2(3)

between the groups on aluminum and sulfur are on the order of 3.4 Å. The average C−Al−C angles for **1**−**6** are in a very narrow range between 119.6° and 121.8°. In **7** this angle opens up to 129.7°. In the dimers, **1**−**3**, the endocyclic angles are all near 90°. In the trimers, **4**−**6**, these angles range from 115° to 122° for Al−S−Al and from 89° to 100° for S−Al−S. In the seat of the chair, the angles at aluminum are 100° and those at sulfur are slightly larger at 115°. The angles at the other positions differ substantially with those around the aluminum at 89° and around sulfur at 122°. In **7** there are substantial changes with all S−Al−S angles near 90° and those around sulfur averaging 128.6°. In the tetrameric structures, the rings have even more flexibility, and the shortest nonbonded interactions are typically 3.5 Å or greater for carbon on adjacent aluminum and sulfur atoms. The endocyclic angles around the ring are 93° to 100° at the metal and 126° to 130° at the sulfur.

It is apparent from these observations that large groups which give rise to significant interactions between groups on adjacent atoms in the ring favor dimers. This, along with the entropy which favors dimers over higher aggregates, takes precedence. When the steric requirements are reduced, the larger aggregates may form. These may be enhanced by reduction of transannular interactions such as axial−axial interactions. The substantial number of these interactions and the lack of information on force constants for deformation of the molecular units make quantitative prediction of the aggregation states difficult. This is further complicated in the solid state by the inclusion of lattice energies which may favor a single conformation or aggregation state. In a paper to follow we will provide a detailed discussion of the behavior of these compounds in solution in which we show that the difference in energy between dimers and trimers is often very small and also describe the flexibility of the rings in solution.

It is interesting to consider the groups that give rise to dimers, trimers, and tetramers. In the dimeric systems, the bridging chalcogen atoms are bound to a variety of groups, i.e., Et, Bu, Ph, and SiPh$_3$. In the observed trimeric aluminum derivatives, the substituents on the bridging atoms are all phenyl groups with substituents on the 2- or 2- and 6-positions. The substituents on the metal are methyl groups in all but one compound where isobutyl groups are present. In the tetramers, very small groups, OH, or large 2,6-Me$_2$C$_6$H$_3$ groups are bound to the chalcogen, and methyl groups are bound to the metal. From these observations, one may conclude that the substituent on the chalcogen may have some influence on the aggregate formed, but the most important contributions appear

Table 14. Selected Structural Data on Aluminum and Gallium Thiolates and Related Compounds

	M−S distance (Å) (av)	S−M−S (deg)	M−S−M (deg)	sum of angles around S
	Aluminum Derivatives			
$[\mathrm{Mes_2Al}(\mu\mathrm{-SBz})]_2$ (**1**)[a]	2.381	89.1	90.9	305.99
$[\mathrm{Me_2Al}(\mu\mathrm{-SSiPh_3})]_2$ (**2**)[a]	2.363	87.5, 87.7	91.9	330.2
			92.5	330.7
$[\mathrm{Mes_2Al}(\mu\mathrm{-SPh})]_2$ (**3**)[a]	2.395	86.4	92	319.5
				313.5
$\{\mathrm{Me_2Al}[\mu\mathrm{-S}(2\text{-}t\text{-}\mathrm{BuC_6H_4})]\}_3$ (**4**)[a]	2.35	100.6	115.1	323.9
		88.8	123.2	338.5
		99.1	114.6	324.6
$\{\mathrm{Me_2Al}[\mu\mathrm{-S(2\text{-}Me_3Si)C_6H_4}]\}_3$ (**5**)[a]	2.36	100.84	120.13	335.73
		89.35	113.53	320.63
		99.20	114.85	326.45
$\{\mathrm{Me_2Al}[\mu\mathrm{-S}(2\text{-}i\text{-}\mathrm{PrC_6H_4})]\}_3$ (**6**)[a]	2.36	101.5	115.8	324.5
		99.9	114.2	337.1
		90.2	122.5	320.0
$\{i\text{-}\mathrm{Bu_2Al}[\mu\mathrm{-S}(2,4,6\text{-}i\text{-}\mathrm{Pr_3C_6H_2})]\}_3$ (**7**)[a]	2.37	89.1	127.6	360.0
		93.2	126.8	357.4
		96.1	131.5	356.3
$\{\mathrm{Me_2Al}[\mu\mathrm{-S(2,6\text{-}Me_2C_6H_3)}]\}_4$ (**8**)[a]	2.363	99.5	126.9	342.8
		94.6	130.7	348.3
$[\mathrm{Me_2Al}(\mu\mathrm{-SMe})]_\infty$ (solid state)[b]	2.348	100.1	103.0	310.3
$[\mathrm{Me_2Al}(\mu\mathrm{-SMe})]_2$ (gas phase)[c]	2.370	85.5	94.5	
$[\mathrm{Me_2Al}(\mu\mathrm{-SC_6F_5})]_2$[d]	2.402	89.4	86.9	301.0
		89.6	87.3	308.0
$\mathrm{Me_3Al{\cdot}SMe_2}$ (gas phase)[e]	2.55			
$[\mathrm{Me_2Al}(\mu\mathrm{-PyS})]_2$[f]	2.338	97.34		
$\mathrm{Al[S}(2,4,6\text{-}t\text{-}\mathrm{Bu_3C_6H_2)]_3}$[g]	2.185	119.8		
	Gallium Derivatives			
$[\mathrm{Ph_2Ga}(\mu\mathrm{-SEt})]_2$[h]	2.373	93.58	86.42	294.92
$[t\text{-}\mathrm{Bu_2Ga}(\mu\mathrm{-SH})]_2$[i]	2.433	90.5	89.5	282.5
$[\mathrm{Me_2Ga}(\mu\mathrm{-SC_6F_5})]$[j]	2.449	89.45	87.75	302.55
		88.59	87.99	304.99
$[\mathrm{I_2Ga}(\mu\mathrm{-SMe})]_2$[k]	2.379	94.5	85.5	
$[\mathrm{I_2Ga}(\mu\text{-S-}i\text{-}\mathrm{Pr})]_2$[l]	2.329	89.1	84.7	
$[t\text{-}\mathrm{BuGa}(\mu_3\mathrm{-S})]_4$[m]	2.359	97.3	82.1	
$\mathrm{Ga[S}(2,4,6\text{-}t\text{-}\mathrm{Bu_3C_6H_2)]_3}$[n]	2.205	119.8		
$\{\mathrm{Me_2Ga}[\mu\mathrm{-S(2,6\text{-}Me_2C_6H_3)}]\}_4$ (**9**)[a]	2.397	93.07	126.21	340.71
		96.6	129.8	346.0

[a] This work. [b] Reference 31. [c] Reference 45. [d] Reference 14. [e] Reference 56. [f] Reference 54. [g] Reference 11. [h] Reference 16. [i] Reference 17. [j] Reference 46. [k] Reference 57. [l] Reference 47. [m] References 15 and 17. [n] Reference 11.

to come from the substituents on the metal with methyl groups favoring formation of larger aggregates. Work is now in progress to determine if it is possible to predict the degree of aggregation by consideration of the substituents on the metal and chalcogen atoms in these cyclic derivatives.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for the support of this research.

Supplementary Material Available: Complete listings of crystal and X-ray data collection parameters, bond distances and angles, anisotropic thermal parameters for the non-hydrogen atoms, and atomic coordinates and isotropic thermal parameters for the hydrogen atoms (41 pages). Ordering information is given on any current masthead page.

OM950150W