Synthesis and Characterization of Aluminum and Gallium Complexes of Heterocyclic Carboxaldehyde Thiosemicarbazones. Single-Crystal Structure of [(MeAl){$NC_4H_3CHNNC(S)N^iC_3H_7$}($AlMe_2$)]$_2$ and $(GaMe_2)_2[SC_4H_3CHNNC(S)NPh]$

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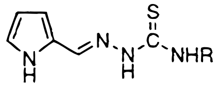
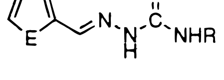
Novel tetranuclear metal complexes with the formula [(MeM){$NC_4H_3CHNNC(S)NR$}(MMe_2)]$_2$ (M = Al, R = $^iC_3H_7$ (**1**); M = Ga, R = $^iC_3H_7$ (**2**); M = Al, R = Me (**3**); M = Ga, R = Me (**4**)) result when pyrrolecarboxaldehyde thiosemicarbazone ligands are mixed with trimethylaluminum and -gallium. Four dinuclear metal compounds with the formula $(MMe_2)_2[SC_4H_3CHNNC(S)NR]$ (M = Al, R = $^iC_3H_7$ (**5**); M = Ga, R = $^iC_3H_7$ (**6**); M = Al, R = C_6H_5 (**7**); M = Ga, R = C_6H_5 (**8**)) were synthesized by the methane elimination reaction of thiophenecarboxaldehyde thiosemicarbazones with trimethylaluminum and -gallium. The X-ray crystal structures of **1** and **8** are described. The structural data revealed that **1** is a tetranuclear aluminum compound with an eight-membered ring system and **8** is a dinuclear gallium compound with a weak interaction between the pendant thiophene and the gallium center.

Introduction

Thiosemicarbazones have been extensively studied for activity against bacterial[1] and viral[2] infections, tuberculosis,[3] rheumatism,[4] and leprosy.[5] Interest in thiosemicarbazone complexes has been stimulated by their biological activity.[6] In particular, gallium(III) complexes of heterocyclic carboxaldehyde thiosemicarbazones continue to attract attention due to the fact that the $^{67}Ga/^{68}Ga$ may offer a convenient source of γ−ray emitters for position emission tomography imaging in institutions which do not have a site cyclotron.[7] Although the coordination chemistry of heterocyclic carboxaldehyde thiosemicarbazones with gallium remains relatively unexplored, Keppler and co-workers[8] recently developed gallium complexes employing ligands which themselves had antiviral and antitumor activity. We have prepared a series of dinuclear group 13 heterocyclic carboxaldehyde thiosemicarbazone complexes, $(Me_2M)_2[NC_5H_4CMeNNC(S)NR]$ (M = Al, Ga; R = Me, $^iC_3H_7$, Ph),[9] and trinuclear aluminum and gallium complexes of bis(thiosemicarbazones).[10] However, the coordination chemistry of the functionalized thiosemicarbazone system with novel substitution patterns remains unexplored. We have decided to investigate the coordination ability of pyrrolecarboxaldehyde thiosemicarbazones (L_1**)** which contain a thiol group or, alternatively, the donor entity HNC=S and pyrrole N−H bond that should be useful for the construction of polynuclear complexes. These ligands attracted our attention because their influence on biological action was observed when the structure of 2-formylpyridine thiosemicarbazone was modified as follows: (1) the pyridine moiety was replaced by another heterocyclic ring and (2) the thiocarbonyl group was replaced by a carbonyl group. In addition, we are interested in conducting a systematic study of the use of terdentate ligands obtained by replacing the pyridine moiety with the thiophene (L_2) and furan moieties (L_3). Our interest in preparing intramolecularly base-coordinated com-



L_1



L_2 = S, L_3 = O

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pounds of Al and Ga was to see to what extent alkyl species would coordinate additional ligands if the donor sites were constrained to lie close to or within the primary coordination sphere. As part of our continuing studies on the synthetic utility and understanding of the uncommon coordination geometry of these ligands with aluminum and gallium, we attempted to synthesize a variety of aluminum and gallium complexes. We now report the synthesis and characterization of group 13 complexes of heterocyclic carboxaldehyde thiosemicarbazone and the single-crystal X-ray structures of three of these.

Experimental Section

General Procedures. All experiments were performed in a dry nitrogen atmosphere using standard Schlenk techniques. Toluene and hexane were distilled under an atmosphere of nitrogen from sodium benzophenone ketyl. AlMe$_3$ and GaMe$_3$ were purchased from Strem Chemicals. 4-Alkyl-3-thiosemicarbazide (H$_2$NNHC(S)NHR) and pyrrole-2-carboxaldehyde were purchased from Aldrich Chemicals and used without further purification. Pyrrolecarboxaldehyde thiosemicarbazones were prepared from the condensation reaction of pyrrole-2-carboxaldehyde and 4-alkyl-3-thiosemicarbazide according to published procedures or slight adaptations thereof.[11]

^{1}H,^{13}C, and ^{27}Al NMR spectra were collected using a Bruker WH-300 spectrometer. The ^{1}H and ^{13}C chemical shifts were referenced to benzene-d_6 (^{1}H, 7.16; ^{13}C{H}, 128.00), while aqueous Al(NO$_3$)$_3$ was used as the ^{27}Al external reference. IR spectra were collected using a Shimadzu FT-IR 8501 spectrometer. Mass spectra were collected using a high-resolution VG70-VSEG spectrometer. Elemental analyses were performed by the Basic Science Center (Seoul, Korea).

General Synthesis of [(MeM){NC$_4$H$_3$CHNNC(S)NR}-(MMe$_2$)]$_2$. In a typical synthesis, trimethylaluminum or -gallium (3 mmol) in toluene (10 mL) was added dropwise to a stirred suspension of L$_1$ (1.5 mmol) in toluene (10 mL) at room temperature. The reaction mixture immediately turned yellow or orange. Slow warming of the mixture to 40−50 °C resulted in gas evolution. The mixture was stirred for 2 h at that temperature until no further gas evolution was observed, and then the solvent was reduced to ca. 5 mL. A 2 mL volume of hexane was layered on this solution and then set aside in the freezer (0 °C) for 2 days to give yellow crystals in 80−85% yield.

[(MeAl){NC$_4$H$_3$CHNNC(S)N^{i}C$_3$H$_7$}(AlMe$_2$)]$_2$ (1). Mp: 210−212 °C. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 7.38 (s, 1H, C*H*), 6.85 (d, 1H, *Py*), 6.57 (m, 1H, *Py*), 6.33 (m, 1H, *Py*), 4.31 (sept, J = 6.32 Hz, 1H, C*H*), 1.02 (d, J = 6.32 Hz, 6H, C*H$_3$*), 0.06 (s, 6H, AlC*H$_3$*), −0.04 (s, 3H, AlC*H$_3$*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C): δ 169.60 (*C*S), 139.12 (H*C*N), 137.31, 129.99, 124.58, 115.22, 24.01 (*C*HCH$_3$), 23.13 (CH*C*H$_3$), - 6.86 (Al*C*H$_3$), −7.91 (Al*C*H$_3$). ^{27}Al NMR: δ 154 ($\omega_{1/2}$ = 2382 Hz), 112 ($\omega_{1/2}$ = 2038 Hz). IR (on KBr pellet; cm^{-1}): 3308 (br), 2954 (m), 1618 (m), 1536 (s), 1472 (m), 1394 (w), 1342 (w), 1302 (w), 1244 (m), 1176 (w), 1125 (w), 1076 (w), 1046 (w), 982 (w), 882 (w), 826 (w), 758 (m), 676 (w), 652 (w), 652 (w), 624 (w), 582 (w), 552 (w), 526 (w). MS(EI): *m/z* 613 [M$^+$], 598 [M$^+$ − CH$_3$]. Anal. Calcd for C$_{24}$H$_{40}$N$_8$S$_2$ Al$_4$: C, 47.05; H, 6.58. Found: C, 46.56; H, 6.32.

[(MeGa){NC$_4$H$_3$CHNNC(S)N^{i}C$_3$H$_7$}(GaMe$_2$)]$_2$ (2). Mp: 190−192 °C dec. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 7.28 (s, 1H, C*H*), 6.58 (m, 1H, *Py*), 6.15 (m, 1H, *Py*), 6.02 (m, 1H, *Py*), 4.28 (sept, J = 6.51 Hz, 1H, C*H*), 1.13 (d, J = 6.51 Hz, 6H, C*H$_3$*), 0.11 (s, 6H, GaC*H$_3$*), −0.15 (s, 3H, GaC*H$_3$*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C): δ 175.17 (*C*S), 137.26 (H*C*N), 133.56, 125.64, 123.23, 114.05, 24.47 (*C*HCH$_3$), 22.46 (CH*C*H$_3$), −3.30 (Ga*C*H$_3$), −4.88 (Ga*C*H$_3$). IR (on KBr pellet; cm^{-1}): 3328 (br), 2962 (m), 2882 (sh), 1616 (m), 1547 (w), 1522 (s), 1454 (m), 1438 (w), 1402 (w), 1374 (m), 1298 (w),1282 (m), 1222 (sh), 1202 (s), 1176 (w), 1122 (w), 1078 (w), 1042 (m), 1020 (w), 990 (w), 972 (w), 882 (w), 836 (w), 752 (m), 672 (w), 580 (w). MS(EI): *m/z* 784 [M$^+$], 769 [M$^+$ − CH3]. Anal. Calcd for C$_{24}$H$_{40}$N$_8$S$_2$Ga$_4$: C, 36.78; H, 5.15. Found: C, 36.22; H, 5.37.

[(MeAl){NC$_4$H$_3$CHNNC(S)NCH$_3$}(AlMe$_2$)]$_2$ (3). Mp: 198−200 °C dec. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 7.42 (s, 1H, C*H*), 6.77 (s, 1H, *Py*), 6.48 (m, 1H, *Py*), 6.29 (m, 1H, *Py*), 2.11 (s, 3H, NC*H$_3$*), 0.07 (s, 6H, AlC*H$_3$*), −0.58 (s, 3H, AlC*H$_3$*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C): δ 172.77 (*C*S), 141.46 (H*C*N), 128.08, 123.22, 120.63, 115.86, 30.16 (N*C*H$_3$), −2.74 (Al*C*H$_3$), −4.62 (Al*C*H$_3$). ^{27}Al NMR: δ 158.38 ($\omega_{1/2}$ = 2274 Hz), 123.82 ($\omega_{1/2}$ = 2078 Hz). IR (on KBr pellet; cm^{-1}): 3242 (m), 2932 (m), 1618 (m), 1558 (m), 1526 (sh), 1455 (w), 1412 (w), 1402 (m), 1332 (w), 1306 (w), 1282 (sh), 1222 (w), 1186 (w), 1114 (w), 1088 (w), 1062 (m), 1044 (sh), 908 (w), 882 (w), 860 (w), 816 (w), 752 (m), 722 (w), 686 (w). MS(EI): *m/z* 557 [M$^+$]. Anal. Calcd for C$_{20}$H$_{32}$N$_8$S$_2$Al$_4$: C, 43.16; H, 5.80. Found: C, 42.66; H, 5.42.

[(MeGa){NC$_4$H$_3$CHNNC(S)NCH$_3$}(GaMe$_2$)]$_2$ (4). Mp: 185−187 °C. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 7.42 (s, 1H, C*H*), 6.55 (m, 1H, *Py*), 6.35 (m, 1H, *Py*), 6.15 (m, 1H, *Py*), 2.25 (s, 3H, NC*H$_3$*), 0.19 (s, 6H, GaC*H$_3$*), −0.26 (s, 3H, GaC*H$_3$*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C): δ 170.88 (*C*S), 137.88 (H*C*N), 127.31, 125.64, 118.01, 110.80, 30.16 (N*C*H$_3$), −2.96 (Ga*C*H$_3$), −4.86 (Ga*C*H$_3$). IR (on KBr pellet; cm^{-1}): 3252 (m), 3154 (m), 3002 (w), 2948 (m), 1617 (m), 1556 (m), 1522 (m), 1436 (w), 1402 (w), 1380 (w), 1378 (w), 1312 (w), 1272 (m), 1224 (sh), 1192 (m), 1168 (w), 1082 (w), 1064 (w), 1042 (m), 1025 (m), 974 (w), 938 (w), 888 (w), 806 (m), 756 (m), 726 (m), 702 (w). MS(EI): *m/z* 727 [M$^+$]. Anal. Calcd for C$_{20}$H$_{32}$N$_8$S$_2$Ga$_2$: C, 33.02; H, 4.43. Found: C, 33.42; H, 4.68.

(AlMe$_2$)$_2$[SC$_4$H$_3$CHNNC(S)N^{i}C$_3$H$_7$] (5). To a stirred suspension of thiophenecarboxaldehyde *N*-isopropylthiosemicarbazone (0.30 g 1.32 mmol) in toluene (10 mL) was added trimethylaluminum (0.19 g, 2.64 mmol) in toluene (10 mL) at −78 °C. The mixture was warmed to room temperature, and heating at 50−70 °C was continued for 12 h. A color change from yellow to orange was observed. The solution was filtered, and the volume was reduced to 5 mL. Hexane (5 mL) was layered on the solution and cooled to −10 °C. Orange crystals were collected by decanting the mother liquor. Yield: 0.35 g (78%). Mp: 148 °C. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 7.85 (s, 1H, C*H*), 6.64 (d, 1H), 6.49 (d, 1H), 6.33 (m, 1H, CH$_{\text{thiop}}$), 4.08 (sept, J = 6.34 Hz, 1H, C*H*), 1.14 (d, J = 6.34 Hz, 6H, C*H$_3$*), 0.08 (s, 6H, AlC*H$_3$*), −0.09 (s, 6H, AlC*H$_3$*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 176.79 (*C*S), 141.20 (H*C*N), 135.67, 132.93, 132.69, 127.71, 50.82 (*C*HCH$_3$), 23.65 (CH*C*H$_3$), −0.01 (Al*C*H$_3$), −8.02 (Al*C*H$_3$). IR (on KBr pellet; cm^{-1}): 3215 (m), 2988 (s), 2920 (m), 1591 (m), 1542 (s), 1469 (s), 1422 (w), 1371 (m), 1338 (w), 1226 (s), 1170 (w), 1152 (w), 1100 (w), 1050 (w), 1027 (w), 992 (w), 927 (w), 859 (w), 838 (w), 690 (br), 571 (w), 490 (w), 461 (w), 524-(w). MS(EI): *m/z* 339 [M$^+$]. Anal. Calcd for C$_{13}$H$_{23}$N$_3$S$_2$Al$_2$: C, 46.00; H, 6.83. Found: C, 45.74; H, 6.88.

(GaMe$_2$)$_2$[SC$_4$H$_3$CHNNC(S)N^{i}C$_3$H$_7$] (6). This compound was obtained in 72% yield by following the same procedure as described for **5**. Mp: 154 °C. ^{1}H NMR (C$_6$D$_6$): δ 7.78 (s, 1H, C*H*), 6.65 (d, 1H), 6.48 (d, 1H), 6.39 (m, 1H, C*H*$_{\text{thiop}}$, 4.28 (sept, J = 6.62 Hz, 1H, C*H*), 1.13 (d, J = 6.62 Hz, 6H, C*H$_3$*), 0.32 (s, 6H, GaC*H$_3$*), 0.01(s, 6H, GaC*H$_3$*). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 178.22 (*C*S), 144.78 (H*C*N), 136.22, 133.42, 132.48, 129.21, 51.44 (*C*HCH$_3$), 25.11 (CH*C*H$_3$), 0.12 (Ga*C*H$_3$), −0.98 (Ga*C*H$_3$). IR (on KBr pellet; cm^{-1}): 3211 (w), 2990 (m), 1588 (w), 1519 (s), 1473 (s), 1431 (w), 1370 (w), 1375 (w), 1298 (w), 1273 (m), 1249 (w), 1222 (w), 1209 (m), 1173 (w), 1100 (w), 1053 (w), 1025 (w), 826 (w), 769 (w), 726 (m), 592 (w), 542 (w), 428 (w). Anal. Calcd for C$_{13}$H$_{23}$N$_3$S$_2$Ga$_2$: C, 36.75; H, 5.46. Found: C, 36.44; H, 5.24.

(AlMe$_2$)$_2$[SC$_4$H$_3$CHNNC(S)NPh] (7). This compound was obtained by following the same procedure as described for **5**

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in 82% yield. Mp: 158 °C. ^{1}H NMR (C_6D_6): δ 7.34 (s, 1H, C*H*), 7.32−6.52 (m, 8H), −0.32 (s, 6H, AlC*H₃*), −0.40 (s, 6H, AlC*H₃*). ^{13}C{^{1}H} NMR (C_6D_6): δ 178.32 (*C*S), 163.68 (*C*N), 160.54, 141.92 140.22, 135.78, 132.68, 131.55, 130.44, 126.08, 125.92, 0.14 (Al*C*H₃), −0.74 (Al*C*H₃). IR (on KBr pellet; cm^{-1}): 3106 (w), 2954 (w), 1595 (w), 1542 (s), 1523 (s), 1491 (s), 1450 (w), 1423 (w), 1375 (w), 1319 (w), 1299 (w), 1254 (m), 1225 (w), 1197 (m), 1094 (w), 1078 (w), 1042 (w), 978 (w), 922 (w), 855 (w), 840 (w), 752 (w), 715 (s), 672 (sh), 638 (w), 575 (w), 520 (w), 491 (w), 469 (w), 422 (w). MS(EI): *m/z* 373 [M$^+$]. Anal. Calcd for $C_{16}H_{21}N_3S_2Al_2$: C, 51.46; H, 5.67. Found: C, 51.22; H, 5.54.

$(GaMe_2)_2[SC_4H_3CHNNC(S)NPh]$ (8). This compound was obtained by following the same procedure as described for **5** in 68% yield. Mp: 160 °C. ^{1}H NMR(C_6D_6): δ 7.84 (s, 1H, C*H*), 7.45−6.37 (m, 8H), 0.31 (s, 6H, GaC*H₃*), 0.11 (s, 6H, GaC*H₃*). ^{13}C{^{1}H} NMR (C_6D_6): δ 180.36 (*C*S), 164.74 (*C*N), 161.92, 144.72, 143.04, 140.76, 136.22, 133.18, 131.54, 131.78, 130.84, 127.22, 126.42, 0.16 (Ga*C*H₃), −0.22 (Ga*C*H₃). IR (on KBr pellet; cm^{-1}): 3216 (w), 2982 (w), 1600 (w), 1496 (s), 1425 (w), 1390 (w), 1320 (m), 1250 (m), 1200 (w), 1073 (w), 1050 (w), 973 (w), 933 (w), 852 (w), 753 (w), 718 (s), 589 (m), 542 (w), 528 (w). Anal. Calcd for $C_{16}H_{21}N_3S_2Ga_2$: C, 41.88; H, 4.61. Found: C, 41.62; H, 4.44.

$(GaMe_2)[OC_4H_3CHNNC(S)NHCH_3]$ (9). To a stirred suspension of furancarboxaldehyde *N*-methylthiosemicarbazone (0.40 g, 2.18 mmol) in toluene (15 mL) was added trimethylgallium (0.34 g, 3.00 mmol) in toluene (10 mL). The reaction mixture was stirred for 1 h at room temperature and then heated at 50−60 °C for 8 h. A color change from beige to orange was observed. The solution was filtered, and the volume was reduced to 10 mL. Pentane (10 mL) was layered on the solution and cooled to −16 °C. Orange crystals were collected by decanting the mother liquor. Yield: 0.41 g (65%). Mp: 136−138 °C. ^{1}H NMR (C_6D_6): δ 7.98 (s, 1H, C*H*), 6.67 (d, 1H), 5.85 (d, 1H), 5.73 (dd, 2H), 4.42 (br, 1H, N*H*), 2.54 (d, *J* = 5.25 Hz, 3H, N-C*H₃*), 0.31 (s, 6H, Ga-C*H₃*). ^{13}C{^{1}H} NMR (C_6D_6): δ 177.62 (*C*S), 143.48 (H*C*N), 139.22, 134.74, 133.92, 130.36, 20.28 (N-*C*H₃), −3.22 (Ga-*C*H₃). IR (on KBr pellet; cm^{-1}): 3302 (m), 2954 (w), 1608 (w), 1542 (s), 1494 (s), 1463 (m), 1405 (s), 1278 (w), 1255 (m), 1196 (w), 1162 (w), 1018 (m), 935 (w), 882 (w), 842 (w), 658 (m), 588 (m), 542 (w). Anal. Calcd for $C_9H_{14}N_3OSGa$: C, 38.34; H, 4.97. Found: C, 38.10; H, 4.72.

$(GaMe_2)_2[OC_4H_3CHNNC(S)NCH_3]$ (10). Compound **10** was prepared using the same procedure as described for **9** from furancarboxaldehyde *N*-methylthiosemicarbazone (0.30 g, 1.64 mmol) and trimethylgallium (0.46 g, 4.06 mmol) in 62% yield. Mp: 118 °C. ^{1}H NMR (C_6D_6): δ 7.57 (s, 1H, C*H*), 7.16 (d, 1H), 6.71 (d, 1H), 6.47 (dd, 2H), 3.2 (s, 3H, N-C*H₃*), −0.02 (s, 6H, Ga-C*H₃*), −0.36 (s, 6H, Ga-C*H₃*). ^{13}C{^{1}H} NMR (C_6D_6): δ 179.06 (*C*S), 144.78 (H*C*N) 141.72, 135.17, 134.04, 131.22, 29.84 (N-*C*H₃), −2.84 (Ga-*C*H₃), −5.34 (Ga-*C*H₃). Anal. Calcd for $C_{11}H_{19}N_3OSGa_2$: C, 34.71; H, 4.99. Found: C, 34.48; H, 4.76.

X-ray Structure Analysis of Compounds 1, 8, and 9. Crystals of **1** and **8** were grown from toluene−hexane. Diffraction data were collected on a Rigaku/RAXIS IIc area detector by employing graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å) at 228 K for both crystals. Indexing was performed from a series of 1 oscillation images with exposures of 5 min/frame. A total of 1710 reflections of **1** and 3772 reflections of **8** were measured over the following ranges: $0.0 \le 2\theta \le 49.9°$, $-29 \le h \le 29.0$, $0 \le k \le 8$, $-15 \le l \le 15$. Of the reflections measured, a total of 1359 unique reflections of **1** and 2810 reflections of **8** with $F^2 > 3.0\sigma(F^2)$ were used during subsequent structure refinement. The structure was solved by direct methods and refined by full-matrix least-squares techniques based on *F* to minimize the quantity $\sum w(F_o - F_c)^2$, with $w = 1/\sigma^2(F)$. Non-hydrogen atoms were anisotropically refined, and hydrogen atoms were included as constant contributions to the structure factors and were not refined.

Table 1. Crystallographic Data for 1, 8, and 9

	1	**8**	**9**
formula	$C_{24}H_{40}N_8S_2Al_4$	$C_{16}H_{21}N_3S_2Ga_2$	$C_9H_{14}N_3OSGa$
fw	612.68	458.92	282.08
cryst syst	orthorhombic	orthorhombic	monoclinic
space group	*Aba*2	*Pbca*	$P2_1/n$
a (Å)	17.781(1)	18.634(2)	10.2140(6)
b (Å)	20.192(2)	19.7840(2)	8.8267(6)
c (Å)	9.207(1)	10.7540(1)	14.452(2)
β (deg)	90	90	108.58(1)
V (Å^3)	3305.4 (3)	3964.52(6)	1235.0(2)
Z	4	8	4
D_{calcd} (g cm^{-3})	1.23	1.538	1.511
F(000)	1296	1856.00	572.00
radiation	Mo Kα ($\lambda = 0.710\ 69$ Å)	Mo Kα ($\lambda = 0.7107$ Å)	Mo Kα ($\lambda = 0.7107$ Å)
total no. of reflns	1710	3772	2338
no. of reflns obsd	1359	2810	1424
GOF	1.44	1.852	3.051
R_1[a]	0.037	0.037	0.071
wR[a]	0.043	0.048	0.080

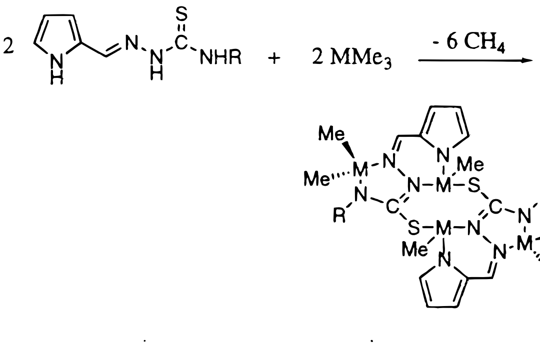
[a] $R_1 = \sum||F_o| - |F_c||/[\sum|F_o|]$; $wR = \{\sum[w(F_o^2 - F_c^2)^2]/[\sum wF_o^2]\}^{1/2}$.

The crystals of **9** were grown from toluene−pentane. Diffraction data were collected on an Enraf-Nonius CAD-4F single-crystal X-ray diffractometer. Unit cell dimensions were determined using 25 machine-centered reflections in the range $17 \le \theta \le 28°$. Reflections were measured with the index ranges $0 \le h \le 9$, $0 \le k \le 13$, $0 \le l \le 22$. The average scan speed was 1 deg min^{-1}, and the $w/2\theta$ scan mode was used for the complex. The structure of the compound was solved using SHELXS-86. Least-squares refinement of scale factors and positional and anisotropic thermal parameters for non-hydrogen atoms was carried out using SHELXS-93. Coordinates of hydrogen atoms were taken from a difference Fourier electron density map and held fixed during refinement. Refinement converged to $R1 = 0.071$ and $R2 = 0.079$.

Crystal data for **1**, **8**, and **9** are summarized in Table 1.

Results and Discussion

The reaction of pyrrolecarboxaldehyde thiosemicarbazones with trimethylaluminum or -gallium in toluene at 40−50 °C affords the corresponding tetranuclear aluminum and gallium complexes, in which six hydrogen atoms have been lost from the aza hydrogen atoms via the methane elimination reaction according to eq 1.



(1)

R = ^{i}C$_3$H$_7$, M = Al (**1**); R = ^{i}C$_3$H$_7$, M = Ga (**2**)
R = CH$_3$, M = Al (**3**); R = CH$_3$, M = Ga (**4**)

The resulting yellow products **1**−**4** were isolated as extremely air-senstive, crystalline solids in high yield. These compounds are readily soluble in benzene, toluene, and THF. Compounds **1**−**4** were characterized by ^{1}H, ^{13}C, and ^{27}Al NMR, mass spectrometry, and elemental analysis. The structure of **1** was determined by

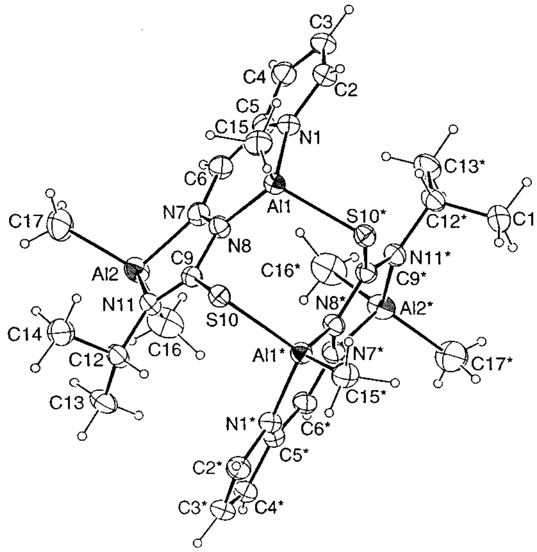


Figure 1. Molecular structure of $[(Me_2Al)_2\{NC_4H_3CHNNC(S)N^iC_3H_7\}(AlMe_2)_2]$ (**1**). Thermal ellipsoids are shown at the 30% probability level.

single-crystal X-ray diffraction. The initial indication of the tetranuclear formulation for **1** stemmed from the observation of a parent ion in the mass spectrum at *m/z* 613, followed by a series of fragmentations attributable to the loss of Me groups. The ^{27}Al NMR spectrum of **1** at room temperature consists of two broad resonances at δ 154 and 112 ppm. The 154 ppm resonance is assigned to the four-coordinate Al(2) in an N_2C_2 coordination environment, which is characteristic of a four-coordinate Al atom when compared with the shift of those in complexes of $[R_2AlR']_2$ (R = Me, Et; R′ = NEt_2, OMe_2, OEt_2, etc).[12] The 112 ppm resonance is assigned to the four-coordinate Al(1). The upfield shifting of the ^{27}Al resonance to δ 92 may be attributed to the greater shielding due to the presence of two N, one S, and one C atoms. The methyl groups of the aluminum moieties give rise to two signals in the ^{1}H NMR spectrum (δ 0.06 and −0.04 ppm) and the ^{13}C NMR spectrum (−6.86 and −7.91 ppm) at 25 °C due to the Al(2)−CH_3 and Al(1)−CH_3 groups, respectively. Examination of the ^{1}H NMR spectrum at −25 °C shows two resonances (δ 0.09 and 0.05 ppm) due to the nonequivalence of the methyl groups on Al(2). In the infrared spectrum of **1**, the stretching mode ν(CS) at 758 cm^{-1} is significantly decreased. This could involve a tautomerism for the semicarbazone-3-thiol, *i.e.*, a 1,3-proton shift. The structures of **2**−**4**, as deduced from ^{1}H and ^{13}C NMR data and elemental analyses, are similar to that of **1**. Although all the spectra are consistent with the proposed formulation, the bonding mode in **1** is still unclear. Accordingly, for confirmation of the structure assignment for **1**, it was necessary to appeal to X-ray crystallography.

Compound **1** crystallizes in the space group *Aba*2 with four molecules per unit cell. The molecular structure and atom numbering schemes for **1** are given in Figure 1. Selected bond distances and angles are given in Table 2. As shown in Figure 1, **1** resides on a crystallographic center of symmetry, with an $Al_2C_2N_2S_2$ eight-membered ring occupying the central cavity of the macrocycle. Furthermore, the molecule consists of a series of two five-membered AlN_3C rings, two six-membered AlN_3C_2 rings, and one eight-membered $Al_2C_2N_2S_2$ ring.

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

Al(1)−S(10*)	2.326(2)	Al(2)−C(17)	1.946(7)
S(10)−C(9*)	1.755(5)	N(1)−C(2)	1.361(6)
Al(1)−N(1)	1.885(4)	N(1)−C(5)	1.388(7)
Al(1)−N(8)	1.902(4)	N(7)−N(8)	1.416(6)
Al(1)−C(15)	1.944(6)	N(7)−C(6)	1.307(6)
Al(2)−N(7)	1.955(4)	N(8)−C(9)	1.362(6)
Al(2)−N(11)	1.910(4)	N(11)−C(9)	1.305(6)
Al(2)−C(16)	1.957(7)	N(11)−C(12)	1.481(6)
Al(1)−S(10*)−C(9*)	98.1(2)	C(2)−N(1)−C(5)	105.1(4)
S(10*)−Al(1)−N(1)	104.8(1)	Al(2)−N(7)−N(8)	122.7(3)
S(10*)−Al(1)−N(8)	112.8(1)	Al(2)−N(7)−C(6)	128.3(4)
S(10*)−Al(1)−C(15)	106.8(2)	N(8)−N(7)−C(6)	118.9(4)
N(1)−Al(1) −N(8)	92.5(2)	Al(1)−N(8)−N(7)	130.0(3)
N(1)−Al(1)−C(15)	110.6(2)	Al(1)−N(8)−C(9)	119.3(3)
N(8)−Al(1)−C(15)	126.7(2)	N(7)−N(8)−C(9)	110.6(3)
N(7)−Al(2)−N(11)	82.3(2)	Al(2)−N(11)−C(9)	113.2(3)
N(7)−Al(2)−C(16)	110.7(3)	Al(2)−N(11)−C(12)	126.0(3)
N(7)−Al(2)−C(17)	109.5(3)	C(9)−N(11)−C(12)	120.8(4)
N(11)−Al(2)−C(16)	112.9(3)	N(1)−C(5)−C(6)	124.2(4)
N(11)−Al(2)−C(17)	114.7(3)	N(7)−C(6)−C(5)	129.0(5)
C(16)−Al(2)−C(17)	120.3(4)	S(10)−C(9)−N(8)	111.8(3)
Al(1)−N(1)−C(2)	129.5(3)	S(10)−C(9)−N(11)	127.1(3)
Al(1)−N(1)−C(5)	125.3(3)	N(8)−C(9)−N(11)	121.1(4)

Several points are worthy of note regarding the structure and bonding in the novel $[(MeAl)\{NC_4H_3CHNNC(S)N^iC_3H_7\}(AlMe_2)]_2$ complex. Compound **1** contains two types of methylaluminum fragments. Two aluminum atoms, Al(2) and Al(2*), have the usual four-coordinate tetrahedral organoaluminum coordination. However, the situation for the remaining aluminum atoms is quite different. The most interesting feature of the molecular structure of **1** is the conformation of the adduct formed and the presence of two chiral Al centers of the same configuration. The Al(1) atom is bridged by one thiolato sulfur atom, forming the eight-membered $Al_2C_2N_2S_2$ ring. The dinuclear aluminum compound in **1**, formed by removing the two hydrogen atoms from the thiol and pyrrole N−H, may be attributed to the strong tendency to form a stable four-coordinate configuration. The N(1)−Al(1)−N(8) angle is restricted by the N(3)−C(2) ring to 92.5(2)°. Because the S(10*)−Al(1)−N(1) and N(8)−Al(1)−C(15) bond angles are 104.8(1)° and 126.7(2)°, respectively, the coordination environment about Al(1) may be described as a distorted tetrahedron. The Al(1)−N(1) distance is 1.885(4) Å. The Al−N bond distance compared well with those in a similar amido DAB compound, $Al(CH_3)_2[N(CH_2CH_2NEt_2)_2]$ (Al−N(amido) = 1.84(1) Å)[13] and a pyridylamido compound, $[AlCl\{NH(8\text{-}C_9H_6N)\}_2]_2$ (Al−N = 1.844(7) Å).[14] The amido Al(1)−N(1) distance is slightly shorter than the imine Al(1)−N(8) bond (1.902(4) Å) and the other pyridyl Al−N bond, indicating that the negatively charged amido nitrogen atom is a stronger donor to the aluminum center than the neutral imine nitrogen atom. The Al(1)−S(10*) distance (2.326(2) Å) is comparable to that observed for the thiolate compound, $AlH(SCH_2CH_2NEt_2)_2$ (2.271(1) Å),[15] the cu-

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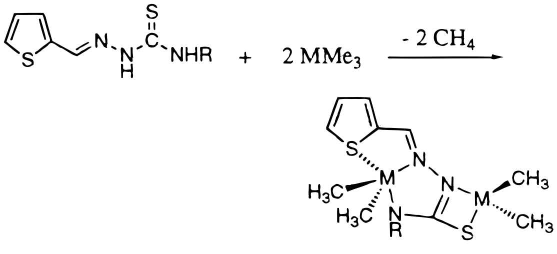
bane compound, $[(^tBu)Al(\mu_3\text{-}S)]_4$ (2.316(9) Å),[16] and the bridged sulfur compound, $[AlMe_2(\mu\text{-}SC_6F_5)]_2$ (2.405 Å).[17] The Al(1)−C(15) bond distance (1.944(6) Å) is typical for four-coordinate aluminum complexes. The other two aluminum atoms, Al(2) and Al(2*), can be described as a distorted tetrahedron. The C(16)−Al(2)−C(17) angle is 120.3(4)°. The methyl ligands are rotated away from nitrogen donor ligands, giving an average C−Al−N angle of 113.8 (3)°. The imine Al(2)−N(7) bond distance (1.955(4) Å) is longer than the amido Al(2)−N(11) distance (1.910(4) Å).

The proximity of the amido nitrogen atom to the aluminum atom appears to be the reason for the asymmetric arrangement. The imine N(8)−C(9) bond distance (1.362(6) Å) is indicative of some double-bond character. The N(7)−N(8) bond distance (1.416(6) Å) is within the realms of those seen for unsubstituted thiosemicabazides (1.411(2) Å)[18] and 4-phenylthiosemicarbazides (1.431(6) Å).[19] The thiolato C(9)−S(10) distance of 1.755(5) Å, which is intermediate between 1.82 Å for a single bond and 1.56 Å for a C=S double bond, agrees with those in related compounds[20] exhibiting thione−thiol tautomerism. The changes in bond distances for the thiocarbamide group [S(10)C(9)N(8)N(11)] indicate that metalation shifts the S(10)−C(9) toward its thiol form, and bond multiplicity shifts from C(9)−N(8) (1.362(6) Å) toward C(9)−N(11) (1.305 (6) Å), probably due to the displacement of the π charge.

The orange crystalline compounds **5**−**8** were prepared via the methane elimination reaction of thiophenecarboxaldehyde thiosemicarbazones with trimethylaluminum or trimethylgallium in toluene at 50−70 °C, as shown in eq 2. Analytical and NMR data of **5**−**8** are consistent with the expected formula. However, in order to reveal the extent to which the SC_4H_3 group is coordinated to the group 13 element centers and to display unusual bonding modes, it was necessary to determine the structure by X-ray crystallography.



(2)

R = $^iC_3H_7$, M = Al (**5**); R = $^iC_3H_7$, M = Ga (**6**)
R = C_6H_5, M = Al (**7**); R = C_6H_5, M = Ga (**8**)

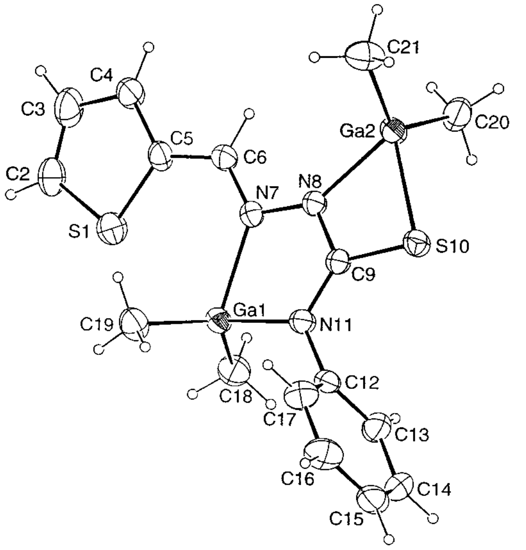


Figure 2. Molecular structure of $(Me_2Ga)_2[SC_4H_3CHNNC(S)NC_6H_5]$ (**8**). Thermal ellipsoids are shown at the 30% probability level.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 8

Ga(1)−N(7)	2.109(3)	Ga(2)−C(20)	1.950(4)
Ga(1)−N(11)	1.968(3)	Ga(2)−C(21)	1.936(5)
Ga(1)−C(18)	1.956(5)	S(10)−C(9)	1.727(4)
Ga(1)−C(19)	1.959(4)	N(7)−N(8)	1.384(4)
Ga(2)−S(10)	2.407(1)	N(7)−C(6)	1.302(4)
Ga(2)−N(8)	2.056(3)	N(8)−C(9)	1.358(4)
Ga(1)−S(1)	3.30		
N(7)−Ga(1)−N(11)	79.2(1)	S(10)−Ga(2)−N(8)	69.27(8)
N(7)−Ga(1)−C(18)	109.4(2)	S(10)−Ga(2)−C(20)	112.8(1)
N(7)−Ga(1)−C(19)	109.9(2)	S(10)−Ga(2)−C(21)	112.4(1)
N(11)−Ga(1)−C(18)	112.1(2)	N(8)−Ga(2)−C(20)	112.0(2)
N(11)−Ga(1)−C(19)	109.7(2)	N(8)−Ga(2)−C(21)	114.5(2)
C(18)−Ga(1)−C(19)	126.5(2)	C(20)−Ga(2)−C(21)	123.5(2)

The structure of **8** is illustrated in Figure 2, and selected bond distances and angles are given in Table 3. The solid state structure of **8** comprises an individual molecule, and there are no unusually short intermolecular contacts between the monomeric units. The molecule consists of a series of four-membered GaNCS rings and five-membered GaN_3C rings. In the solid state, the Ga(2) center is coordinated by one nitrogen, one sulfur, and two methyl groups in a distorted tetrahedral configuration. Significant distortion from an ideal tetrahedral geometry is observed for the gallium atom, Ga(2), in the constrained four-membered ring; the ring angle is 69.27(8)°. The Ga(2)−S(10) bond distance (2.407(1) Å) is slightly longer than that observed for $[Py(^tBu)GaS]_3$ (2.231(3)−2.253(3) Å)[21] and for the thiolate-bridged complexes, $Ga_4I_4(SMe)_4S_2$ (2.204(8) Å).[22] However, the Ga(2)−S(10) and Ga(2)−N(8)(2.056(3) Å) bond distances in **8** are comparable to those of the pyridine-2-thiol complex $Ga(SC_6H_4N)_3$ (Ga−S = 2.420(3) Å; Ga−N = 2.062(8) Å).[23]

The primary coordination sphere of Ga(1) consists of a distorted tetrahedral configuration. However, weak secondary interaction between the pendant thiophene and the gallium center is evident. The orientations of these interactions are such that the ion pairs of the thiophene group are directed toward the gallium center, and the Ga···S vector lies approximately trans to the Ga−N(11) bond, with an S···Ga−N angle of 153.6(3)°. Although the gallium−sulfur distance (3.30 Å) is less than the sum of van der Waals radii for gallium and sulfur (3.70 Å),[24] they exceed typical Ga−S covalent

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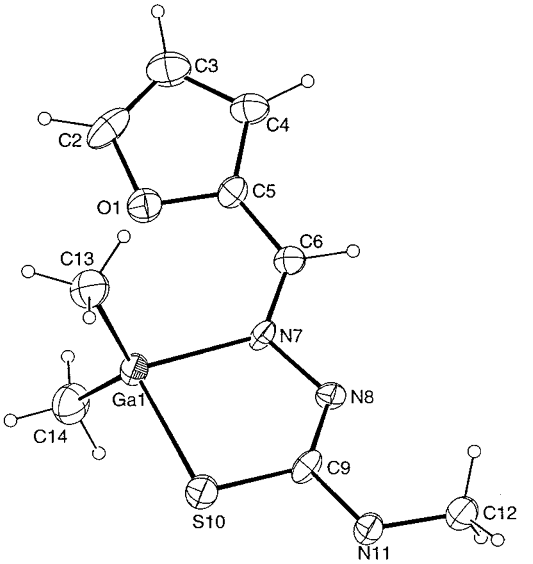
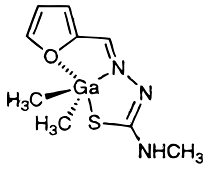


Figure 3. Molecular structure of (GaMe$_2$)[OC$_4$H$_3$CHNNC(S)NHCH$_3$] (**9**). Thermal ellipsoids are shown at the 30% probability level.

bond distances (2.22 Å). If this subsidiary Ga···S interaction is included, the overall geometry at gallium is that of a distorted trigonal bipyramid. Such a weak interaction has been observed previously in group 13 compounds.[25]

The furancarboxaldehyde thiosemicarbazone complexes of trimethylgallium were synthesized using relatively straightforward reactions with toluene as the reaction solvent. Complexes **9** and **10** are orange crystalline solids which are soluble in benzene, toluene, and THF. Satisfactory elemental analytical data were obtained for the compounds. The ^{1}H and ^{13}C NMR spectra of **9** and **10** are consistent with the expected formulas. The ^{1}H and ^{13}C NMR spectra of **10** at 25 °C show two resonances for the methyl groups, demonstrating the presence of the methyl groups in a different environment. The structure of **9** is illustrated in Figure 3, and selected bond distances and angles are given in Table 4. Confirmation of the mononuclear structure of **9** was provided by X-ray crystallography. Compound **9** crystallizes in the space group $P2_1/n$ with four molecules per unit cell. In the previous crystal structure of **8**, any association in the solid via Ga···S interaction is likely to be weak. Oxygen is a stronger Lewis base toward gallium than sulfur. Thus, the Ga−O bonding interactions would be more extensive than Ga−S interactions, resulting in longer Ga−S bond distances. The Ga(1)···O(1) contact (2.88 Å) appears to be weak, having a bond length greater than that normally seen for Ga−O dative bonds. If this subsidiary Ga···O interaction is included, the overall geometry at gallium is that of a distorted trigonal bipyramid. Such interactions have been observed in a number of aluminum compounds.[26]



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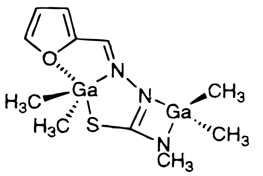

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Table 4. Selected Bond Distances (Å) and Angles (deg) for 9

Ga(1)−S(10)	2.328(3)	N(7)−N(8)	1.40(1)
Ga(1)−N(7)	2.089(7)	N(7)−C(6)	1.29(1)
Ga(1)−C(13)	1.96(1)	N(8)−C(9)	1.31(1)
Ga(1)−C(14)	1.93(1)	N(11)−C(9)	1.35(1)
S(10)−C(9)	1.74(1)	N(11)−C(12)	1.45(1)
Ga(1)−O(1)	2.88		
S(10)−Ga(1)−N(7)	84.1(2)	C(13)−Ga(1)−C(14)	125.7(5)
S(10)−Ga(1)−C(13)	109.8(4)	Ga(1)−S(10)−C(9)	94.8(3)
S(10)−Ga(1)−C(14)	110.4(4)	Ga(1)−N(7)−N(8)	118.3(6)
N(7)−Ga(1)−C(13)	109.8(4)	Ga(1)−N(7)−C(6)	128.1(6)
N(7)−Ga(1)−C(14)	109.2(4)	N(7)−N(8)−C(9)	115.2(7)

The use of the pyrrolecarboxaldehyde thiosemicabazones as ligands in the organometallic chemistry of aluminum and gallium leads to tetranuclear organometallic complexes of these complexes having uncommon bonding modes. X-ray crystallographic studies and spectroscopic parameters confirm that these complexes represent rather unusual four-coordinate geometries. The Ga···S and Ga···O contacts between the pendant thiophene and furan appear to be weak. The Ga···S dative bond is weaker than the Ga···O bond in the corresponding oxygen analogue, agreeing with the basicity series (N > O > S) established for donor compounds of gallium Lewis acids. Consequently, the GaMe$_2$ unit is stabilized by axially positioned Ga···S or Ga···O interaction. We are currently in the process of using these ligands to stabilize low-coordinate main group species. The chemistry of the ligands with hard metal ions of d-block elements is also of interest.

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Supporting Information Available: Tables of bond distances and angles, atomic coordinates, fractional coordinates for hydrogen atom, thermal parameters, and X-ray data for **1, 8**, and **9** (22 pages). Ordering information is given on any current masthead page.

OM970660L

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