Unusual Coordination Chemistry of Organoaluminum and -gallium Complexes in N_2S and NS Coordination Environments. Synthesis and Crystal Structure of $(Me_2Al)[NC_5H_4CMeNNC(S)NC_3H_7](AlMe_2)$ and $(Me_2Ga)[PhMeCNNC(S)NPh](GaMe_2)$

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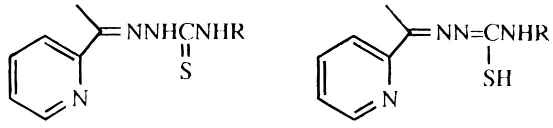
The synthesis and characterization of the dinuclear group 13 heterocyclic carboxaldehyde thiosemicarbazone complexes $(Me_2M)[NC_5H_4CMeNNC(S)NR](MMe_2)$ (M = Al, R = Me (**1**), ${}^iC_3H_7$ (**3**), Ph (**5**); M = Ga, R = Me (**2**), ${}^iC_3H_7$ (**4**), Ph (6)) and acetophenone thiosemicarbazone complexes $(Me_2M)(CH_3RCNNC(S)NR')(MMe_2)$ (M = Al, R = Ph, R′ = Ph (**7**); M = Al, R = CH_3, R′ = CH_3 (**9**); M = Ga, R = Ph, R′ = Ph (**8**); M = Ga R = CH_3, R′ = CH_3 (**10**)) are described. Compounds **1**−**6** were prepared by the reaction of MMe_3 (M = Al, Ga) with 2-acetylpyridine 4-alkylthiosemicarbazone in toluene. Compounds **7**−**10** were prepared using MMe_3 (M = Al, Ga) in toluene with acetophenone 4-alkylthiosemicarbazone under anaerobic conditions. These compounds, **1**−**10**, have been characterized by microanalysis, NMR (${}^1H$, ${}^{13}C$, ${}^{27}Al$) spectroscopy, and single-crystal X-ray diffraction. X-ray single-crystal diffraction analyses reveal that compound **3** is a dinuclear aluminum compound with coordination numbers of five and four and compound **8** is a dinuclear gallium compound in which each gallium atom is four-coordinate.

Introduction

The terdentate heterocyclic carboxaldehyde thiosemicarbazones have been shown to form complexes with various transition-metal ions, including Cu(II),[1] Ni(II),[2] Co(II),[3] Fe(II),[4] Hg(I),[5] and Tl(I).[5] Extensive literature on the antitumor properties of many α-*N*-heterocyclic carboxaldehyde thiosemicarbazones is now available. The gallium(III) complexes of the heterocyclic carboxaldehyde thiosemicarbazones have continued to attract attention due to the fact that the radioactive species of gallium (${}^{67}Ga$) are γ-ray emitters with energies which make them useful as medical diagnostic agents.[6] Recently, Kepper and co-workers[7] developed gallium(III) complexes employing ligands which themselves had antiviral and antitumor activity, such as α-*N*-heterocyclic carboxaldehyde thiosemicarbazones.[8]

Chart 1



I II

We[9] have recently prepared a series of trinuclear group 13 bis(thiosemicarbazone) complexes $(MeM)\{CH_2[C(Me)NNC(S)(NR)]_2\}(MMe_2)_2$ (M = Al, Ga; R = Me, Et, Ph). However, the coordination chemistry of the thiosemicarbazone ligands with aluminum and gallium remains relatively unexplored. We have decided to investigate the coordination ability of the thiosemicarbazone that contains a semicarbazone with one thiol group (Chart 1, **II**) or alternatively one HN−C=S donor entity (**I**), which should be useful for the construction of polynuclear complexes. Since the general type of reaction, namely evolution of an alkane from the interaction of AlR_3/GaR_3 with N−H/S−H bonds, is well-

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established for both the open chain[10] and closed macrocyclic systems,[11] the α-*N*-heterocyclic carboxaldehyde thiosemicarbazone ligand is valuable in the preparation of alkyl complexes of group 13 organometallic species.

Motivated by an interest in the specific effects of the α-*N*-heterocyclic carboxaldehyde thiosemicarbazone geometry on the coordination environments of aluminum and gallium, we began a systematic study of the use of terdentate and acetophenone thiosemicarbazone ligands for organometallic aluminum and gallium compounds. We report here the interaction of trimethylaluminum and -gallium with the *N*,*N*,*S*-terdentate ligand acetylpyridine thiosemicarbazone and the *N*,*S*-bidentate ligand acetophenone thiosemicarbazone.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free, dinitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmosphere HE-493 drybox. Toluene and hexane were freshly distilled from sodium/benzophenone prior to use. All ^{1}H, ^{13}C, and ^{27}Al NMR spectra were measured on a Bruker WH-300 spectrometer. Chemical shifts were referenced relative to either TMS (^{1}H) or benzene-d_6 (^{1}H, δ 7.155; ^{13}C{^{1}H}, δ 128.00), while ^{27}Al NMR spectra were referenced relative to $Al(H_2O)_6^{3+}$. IR spectra were recorded on a Shimadzu FT-IR-8501 spectrometer. Mass spectra were recorded on a high-resolution VG 70-VSEG instrument, and elemental analyses were performed by the Basic Science Center. The ligands $[NC_5H_4CRNNHC(S)NHR']$ ($R = CH_3$; $R' = CH_3$, C_3H_7, C_6H_5) were prepared according to the literature methods.[8d] $AlMe_3$ and $GaMe_3$ were purchased from Strem Chemicals.

General Synthesis of $(Me_2M)[NC_5H_4C(CH_3)NNC(S)NR](MMe_2)$ and $(Me_2M)[PhMeCNNC(S)NR](MMe_2)$. In a typical synthesis, a solution of 2-acetylpyridine 4-methylthiosemicarbazone (2.0 mmol) in toluene (10 mL) was treated with MMe_3 (4 mmol) at room temperature. The stirred mixture was warmed to 35 °C, during which the suspension dissolved. The resulting yellow solution was stirred at that temperature for 2 h and then allowed to cool to 25 °C. The solution was layered with hexane (3 mL) and stored at −15 °C for 1 day, whereupon yellow crystals formed in 85−95% yield.

$(Me_2Al)[NC_5H_4C(CH_3)NNC(S)NMe](AlMe_2)$ (1). Mp: 148 °C (dec). ^{1}H NMR (C_6D_6, 25 °C): δ 7.95 (m, 1H, *Py*), 6.72 (m, 1H, *Py*), 6.35 (m, 1H, *Py*), 6.25 (m, 1H, *Py*), 3.20 (s, 3H, NCH_3), 1.68 (s, 3H, CCH_3), −0.05 (s, 6H, $AlCH_3$), −0.47 (s, 6H, $AlCH_3$). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 189.16 (*C*S), 149.92 ($C(CH_3)N$), 145.94, 143.58, 138.41, 122.10, 119.90 (*C*H, Py), 30.10 (NCH_3), 11.94 (CCH_3), −0.03 ($AlCH_3$), −4.87 ($AlCH_3$). ^{27}Al NMR: δ 153 ($w_{1/2} = 3680$ Hz), 109 ($w_{1/2} = 2544$ Hz). IR (KBr pellet; cm^{-1}): 2946 (w), 1535 (m), 1523 (s), 1508 (sh), 1485 (w), 1450 (w), 1422 (w), 1391 (br), 1287 (w), 1246 (w), 1225 (m), 1160 (w), 1140 (w), 1130 (w), 1097 (w), 1046 (w), 1042 (w), 1035 (w), 983 (w), 829 (w), 774 (m), 735 (w), 640 (br). Anal. Calcd for $C_{13}H_{22}N_4SAl_2$: C, 48.74; H, 6.92. Found: C, 48.42; H, 6.88.

$(Me_2Ga)[NC_5H_4C(CH_3)NNC(S)NMe](GaMe_2)$ (2). Mp: 168 °C. ^{1}H NMR (C_6D_6, 25 °C): δ 7.85 (m, 1H, *Py*), 6.81 (m, 1H, *Py*), 6.48 (m, 1H, *Py*), 6.39 (m, 1H, *Py*), 3.18 (s, 3H, NCH_3), 1.75 (s, 3H, CCH_3), 0.33 (s, 6H, $GaCH_3$), −0.09 (s, 6H, $GaCH_3$). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 175.84 (*C*S), 148.94 ($C(CH_3)N$), 145.84, 137.91, 137.24, 122.99, 120.43 (*C*H, Py), 31.90 (NCH_3), 14.28 (CCH_3), −1.31 ($GaCH_3$), −6.07 ($GaCH_3$). IR (KBr pellet; cm^{-1}): 2983 (br), 1581 (w), 1550 (br), 1535 (br), 1485 (br), 1434 (s), 1385 (s), 1370 (sh), 1323 (w), 1282 (w), 1268 (w), 1227 (s), 1179 (s), 1148 (m), 1135 (w), 1102 (m), 1081 (w), 1037 (w), 1006 (w), 971 (w), 860 (w), 828 (s), 770 (s), 740 (m), 729 (w), 676 (w), 631 (w). MS (EI): *m/z* 405 [M$^+$], 206 [M$^+$ − 4GaMe$_3$]. Anal. Calcd for $C_{13}H_{22}N_4SGa_2$: C, 38.47; H, 5.47. Found: C, 38.29; H, 5.28.

$(Me_2Al)[NC_5H_4C(CH_3)NNC(S)NC_3H_7](AlMe_2)$ (3). Mp: 139 °C (dec). ^{1}H NMR (C_6D_6, 25 °C): δ 7.93 (m, 1H, *Py*), 6.70 (m, 1H, *Py*), 6.27 (m, 2H, *Py*), 4.29 (sept, $J = 6.48$ Hz, 1H, C*H*), 1.70 (s, 3H, CH_3), 1.19 (d, $J = 6.48$ Hz, 6H, CH_3), −0.05 (s, 6H, $AlCH_3$), −0.22 (s, 6H, $AlCH_3$). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 185.85 (*C*S), 148.23 ($C(CH_3)N$), 146.02, 139.44, 138.80, 123.17, 119.74 (*C*H, Py), 23.52 (NCH_3), 14.27 ($CHCH_3$), 13.61 ($CHCH_3$), −0.04 ($AlCH_3$), −8.76 ($AlCH_3$). ^{27}Al NMR: δ 152, 114. IR (KBr pellet; cm^{-1}): 2938 (w), 2880 (w), 1590 (w), 1506 (s), 1494 (sh), 1450 (m), 1420 (s), 1373 (w), 1356 (w), 1304 (w), 1289 (w), 1200 (w), 1190 (sh), 1173 (br), 1142 (m), 1112 (w), 1105 (w), 1076 (w), 1041 (w), 1014 (w), 994 (w), 980 (w), 850 (br), 798 (w), 775 (m), 741 (w), 732 (w), 650 (w). Anal. Calcd for $C_{15}H_{26}N_4SAl_2$: C, 51.71; H, 7.52. Found: C, 51.34; H, 7.38.

$(Me_2Ga)[NC_5H_4C(CH_3)NNC(S)NC_3H_7](GaMe_2)$ (4). Mp: 162 °C. ^{1}H NMR (C_6D_6, 25 °C): δ 7.94 (m, 1H, *Py*), 6.83 (m, 1H, *Py*), 6.64 (m, 1H, *Py*), 6.41 (m, 1H, *Py*), 4.41 (sept, $J = 6.36$ Hz, 1H, C*H*), 2.22 (s, 3H, CH_3), 0.95 (d, $J = 6.36$ Hz, 6H, $CH(CH_3)_2$), 0.39 (s, 6H, $GaCH_3$), −0.12 (s, 6H, $GaCH_3$). ^{13}C{1H} NMR (C_6D_6, 25 °C): δ 186.21 (*C*S), 149.67 ($C(CH_3)N$), 144.28, 139.21, 137.91, 123.13, 120.68 (*C*H, Py), 22.63 (NCH_3), 14.66 ($CHCH_3$), 13.14 ($CHCH_3$), −0.03 ($GaCH_3$), −5.24 ($GaCH_3$). IR (KBr pellet; cm^{-1}): 3309 (s), 2940 (w), 2890 (br), 1584 (m), 1499 (w), 1480 (w), 1425, (s), 1322 (w), 1298 (m), 1282 (w), 1232 (s), 1170 (m), 1150 (m), 1140 (w), 1085 (w), 1073 (w), 1040 (w), 881 (w), 850 (m), 820 (m), 772 (m), 760 (w), 740 (br), 662 (w), 636 (w). Anal. Calcd for $C_{15}H_{26}N_4SGa_2$: C, 41.54; H, 5.99. Found: C, 41.22; H, 5.68.

$(Me_2Al)[NC_5H_4C(CH_3)NNC(S)NC_6H_5](AlMe_2)$ (5). Mp: 143 °C (dec). ^{1}H NMR (C_6D_6, 25 °C): δ 7.84 (m, 1H, *py*), 7.52 (m, 2H, *Ph*), 7.25 (m, 2H, *Ph*), 7.03 (m, 1H, *Ph*), 6.72 (m, 1H, *py*), 6.32 (m, 2H, *py*), 1.78 (s, 3H, CH_3), 0.47 (s, 6H, $AlCH_3$), −0.41 (s, 6H, $AlCH_3$). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 175.47 (*C*S), 147.59 ($C(CH_3)N$), 146.35, 145.29, 144.22, 139.13, 127.68, 126.31, 125.63, 124.35, 121.01, 12.76 (CCH_3), −6.11 ($AlCH_3$), −7.79 ($AlCH_3$). IR (KBr pellet; cm^{-1}): 2890 (w), 1580 (m), 1500 (br), 1470 (s), 1427 (s), 1046 (sh), 1376 (w), 1328 (w), 1290 (w), 1256 (w), 1240 (br), 1165 (s), 1095 (w), 1059 (w), 1018 (w), 985 (br), 942 (w), 920 (w), 815 (br), 769 (m), 688 (br), 655 (w). MS (EI): *m/z* 382 [M$^+$], 268 [M$^+$ − 4AlMe$_3$]. Anal. Calcd for $C_{18}H_{24}N_4SAl_2$: C, 56.54; H, 6.28. Found: C, 56.22; H, 5.95.

$(Me_2Ga)[NC_5H_4C(CH_3)NNC(S)NC_6H_5](GaMe_2)$ (6). Mp: 168−172 °C. ^{1}H NMR(C_6D_6, 25 °C): δ 7.35 (m, 1H, *py*), 7.11−7.34 (m, 1H, *Ph*), 6.76−6.87 (m, 3H, *Ph*), 6.62 (m, 1H, *Ph*), 6.13 (m, 1H, *py*), 6.00 (m, 1H, *py*), 1.44 (s, 3H, CH_3), −0.07 (s, 6H, $GaCH_3$), −0.41 (s, 6H, $Ga{-}CH_3$). ^{13}C{^{1}H} NMR (C_6D_6, 25 °C): δ 177.35 (*C*S), 150.78, 148.91, 145.72, 140.72, 138.04, 136.35, 127.68, 125.66, 123.88, 122.83, 121.39, 15.29 (CCH_3), −0.08 ($GaCH_3$), −5.07 ($GaCH_3$). IR (KBr pellet; cm^{-1}): 2939 (w), 1590 (m), 1484 (m), 1445 (m), 1419 (s), 1312 (w), 1249 (m), 1191 (w), 1182 (w), 1149 (m), 1100 (w), 1080 (w), 1068 (w), 1042 (w), 1036 (w), 1010 (br), 946 (w), 892 (w), 854 (w), 832 (w), 812 (w), 775 (m), 746 (m), 740 (sh), 700 (w), 689 (w), 672 (br), 655 (w), 636 (w), 620 (br). Anal. Calcd for $C_{18}H_{24}N_4SGa_2$: C, 46.20; H, 5.13. Found: C, 45.86; H, 4.92.

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(Me_2Al)[MePhCNNC(S)NC_6H_5]($AlMe_2$) (7). Mp: 148 °C. ^{1}H NMR (C_6D_6, 25 °C): δ 7.49 (m, 2H, *Ph*), 7.33 (m, 2H, *Ph*), 7.09−7.16 (m, 4H, *Ph*), 6.91−6.97 (m, 4H, *Ph*), 2.11 (s, 3H, CH_3), −0.07 (s, 6H, $AlCH_3$), −0.71 (s, 6H, $AlCH_3$). $^{13}C\{^1H\}$ NMR(C_6D_6, 25 °C): δ 180.17 (*C*S), 165.61 (*C*N), 161.36, 143.95, 137.23, 131.26, 126.26, 125.79, 22.07 (CH_3), −6.52 ($AlCH_3$), −8.49 ($AlCH_3$). ^{27}Al NMR: δ 148 ($w_{1/2} = 2262$ Hz). IR (KBr pellet; cm^{-1}): 3050 (w), 2825 (w), 1598 (w), 1537 (sh), 1525 (s), 1484 (w), 1449 (w), 1362 (w), 1312 (sh), 1285 (br), 1260 (w), 1182 (m), 1157 (sh), 1103 (w), 1062 (w), 1025 (w), 1000 (w), 975 (w), 930 (w), 793 (w), 764 (m), 730 (w), 694 (w). Anal. Calcd for $C_{19}H_{25}N_3SAl_2$: C, 59.82; H, 6.18. Found: C, 59.51; H, 6.02.

(Me_2Ga)[MePhCNNC(S)NC_6H_5]($GaMe_2$) (8). Mp: 136 °C. ^{1}H NMR (C_6D_6, 25 °C): δ 7.38−7.42 (m, 2H, *Ph*), 7.12−7.17 (m, 4H, *Ph*), 6.92−7.02 (m, 4H, *Ph*), 2.03 (s, 3H, CH_3), 0.31 (s, 6H, $GaCH_3$), −0.33 (s, 6H, $GaCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 178.88 (*C*S), 167.59 (*C*N), 140.65, 138.32, 130.30, 126.47, 125.56, 123.49, 122.94, 122.61, 120.42, 22.73 (CH_3), −1.88 ($GaCH_3$), −5.06 ($GaCH_3$). IR (KBr pellet; cm^{-1}): 2900 (w), 2825 (w), 1595 (w), 1580 (w), 1575 (w), 1510 (sh), 1502 (s), 1491 (s), 1480 (s), 1448 (w), 1368 (w), 1330 (m), 1316 (w), 1280 (w), 1264 (w), 1230 (s), 1203 (w), 1186 (w), 1178 (w), 1151 (w), 1120 (w), 1075 (w), 1052 (w), 1018 (w), 1000 (w), 967 (w), 950 (m), 925 (w), 908 (w), 850 (w), 837 (w), 818 (w), 766 (m), 742 (m), 730 (w), 700 (s), 660 (m), 638 (w), 618 (w). MS (EI): *m/z* 467 [M$^+$], 437 [M$^+$ − 2CH_3]. Anal. Calcd for $C_{19}H_{25}N_3SGa_2$: C, 48.87; H, 5.41. Found: C, 48.38; H, 5.23.

(Me_2Al)[Me_2CNNC(S)NCH_3]($AlMe_2$) (9). Mp: 118−120 °C (dec). ^{1}H NMR (C_6D_6, 25 °C): δ 2.76 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), −0.19 (s, 6H, $AlCH_3$), −0.56 (s, 6H, $AlCH_3$). $^{13}C\{^1H\}$ NMR(C_6D_6, 25 °C): δ 180.24 (*C*S), 158.15 (*C*N), 33.24 (NCH_3), 23.86 (CCH_3), 21.68 (CCH_3), −6.59 ($AlCH_3$), −10.88 ($AlCH_3$). ^{27}Al NMR: δ 150 ($w_{1/2} = 2314$ Hz). IR (KBr pellet; cm^{-1}): 3240 (br), 1550 (s), 1538 (sh), 1475 (m), 1450 (br), 1430 (w), 1404 (w), 1366 (w), 1344 (w), 1267 (m), 1226 (s), 1165 (br), 1103 (w), 1095 (w), 1060 (w), 1044 (w), 1017 (w), 1008 (w), 900 (w), 850 (w), 769 (m), 744 (w), 710 (w), 660 (w). Anal. Calcd for $C_9H_{21}N_3SAl_2$: C, 42.00; H, 8.24. Found: C, 41.62; H, 8.02.

(Me_2Ga)[Me_2CNNC(S)NCH_3]($GaMe_2$) (10). Mp: 64−66 °C. ^{1}H NMR (C_6D_6, 25 °C): δ 2.90 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 0.21 (s, 6H, $GaCH_3$), −0.21 (s, 6H, Ga−CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 179.24 (*C*S), 170.34, 162.33 (*C*N), 33.64 (NCH_3), 23.65 (CCH_3), −3.10 ($GaCH_3$), −7.37 ($GaCH_3$). IR (KBr pellet; cm^{-1}): 2940 (br, w), 2872 (br, w), 1608 (w), 1504 (s), 1485 (s), 1449 (w), 1430 (w), 1393 (m), 1370 (w), 1366 (w), 1280 (w), 1250 (m), 1211 (w), 1198 (w), 1190 (w), 1167 (m), 1156 (w), 1119 (w), 1012 (w), 985 (w), 963 (br, w), 851 (w), 840 (w), 790 (m), 730 (br, w), 699 (br, w), 660 (w). Anal. Calcd for $C_9H_{21}N_3SGa_2$: C, 31.53; H, 6.19. Found: C, 31.14; H, 5.92.

X-ray Crystallography. Details of the crystal data and a summary of intensity data collection parameters for **3** and **8** are given in Table 1. The crystals of **3** and **8** were grown from a toluene/hexane solution at −15 °C. The crystals of **3** and **8** were mounted in thin-walled glass capillaries and sealed under argon. The data sets of **3** and **8** were collected using a Rigaku/RAXIS IIa area detector employing graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 96$ Å) at a temperature of 253 K. The structure were solved by direct methods. Refinements were by full-matrix least-squares techniques based on *F* to minimize the quantity $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. Non-hydrogen atoms of **3** and **8** were anisotropically refined, and hydrogen atoms were isotropically refined. The hydrogen atoms of **3** and **8** were included as constant contributions to the structure factors. The refinement of **3** converged to R1 = 0.068 and wR2 = 0.076 and that of **8** converged to R1 = 0.0425 and wR2 = 0.0566. Selected bond distances and angles for **3** and **8** are given in Tables 2 and 3, respectively. The molecular structure of compounds **3** and **8** are given in Figures 1 and 2, respectively.

Table 1. Crystallographic Data for the Structural Studies of Compounds 3 and 8

	3	8
empirical formula	$C_{15}H_{26}N_4SAl_2$	$C_{19}H_{25}N_3SGa_2$
fw	348.42	466.93
cryst class	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	15.337(3)	12.5180(3)
b, Å	16.951(3)	8.9768(4)
c, Å	8.794(2)	19.1100(6)
α, deg	96.03(1)	
β, deg	91.10(1)	102.700(3)
γ, deg	74.81(1)	
V, Å^3	2194.2(9)	2145.7500
D_c, g cm^{-3}	1.12	1.445
F(000)	744	226
Z	4	4
μ(Mo Kα), cm^{-1}	2.33	
total no. of reflns	6775	16 435
no. of obsd reflns	3695	2797
goodness of fit	2.30	1.53
R1[a]	0.068	0.0425
wR2[a]	0.076	0.0566

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound 3

Al(1)−S(11)	2.491(3)	Al(4)−N(32)	1.913(5)
S(11)−C(10)	1.691(6)	Al(4)−C(39)	1.946(8)
Al(3)−S(31)	2.487(2)	Al(4)−C(40)	1.928(8)
S(31)−C(30)	1.709(5)	N(1)−C(2)	1.339(8)
Al(1)−N(1)	2.076(5)	N(1)−C(6)	1.351(7)
Al(1)−N(8)	2.040(5)	N(8)−N(9)	1.362(6)
Al(1)−C(17)	1.962(7)	N(8)−C(7)	1.320(7)
Al(1)−C(18)	1.947(7)	N(9)−C(10)	1.380(7)
Al(2)−N(9)	1.946(5)	N(12)−C(10)	1.318(7)
Al(2)−N(12)	1.915(5)	N(12)−C(13)	1.463(7)
Al(2)−C(19)	1.953(7)	N(21)−C(22)	1.339(7)
Al(2)−C(20)	1.939(7)	N(21)−C(26)	1.356(7)
Al(3)−N(21)	2.088(5)	N(28)−N(29)	1.349(6)
Al(3)−N(28)	2.057(5)	N(28)−C(27)	1.299(6)
Al(3)−C(37)	1.951(7)	N(29)−C(30)	1.380(7)
Al(3)−C(38)	1.977(7)	N(32)−C(30)	1.309(7)
Al(4)−N(29)	1.953(5)	N(32)−C(33)	1.466(7)

Al(1)−S(11)−C(10	95.7(2)	N(12)−Al(2)−C(20)	115.9(3)
S(11)−Al(1)−N(1)	156.5(2)	C(19)−Al(2)−C(20)	118.0(3)
S(11)−Al(1)−N(8)	80.1(2)	Al(1)−N(1)−C(2)	124.8(4)
S(11)−Al(1)−C(17)	97.4(2)	Al(1)−N(1)−C(6)	116.4(4)
S(11)−Al(1)−C(18)	97.1(2)	C(2)−N(1)−C(6)	118.8(5)
N(1)−Al(1)−N(8)	76.4(2)	Al(1)−N(8)−N(9)	123.6(4)
N(1)−Al(1)−C(17)	94.5(3)	Al(1)−N(8)−C(7)	118.5(4)
N(1)−Al(1)−C(18)	93.8(3)	N(9)−N(8)−C(7)	117.8(5)
N(8)−Al(1)−C(17)	119.6(3)	Al(2)−N(9)−N(8)	151.5(4)
N(8)−Al(1)−C(18)	118.6(3)	Al(2)−N(9)−C(10)	91.6(4)
C(17)−Al(1)−C(18)	121.5(3)	N(8)−N(9)−C(10)	116.7(5)
N(9)−Al(2)−N(12)	67.7(2)	Al(2)−N(12)−C(10)	94.9(4)
N(9)−Al(2)−C(19)	113.2(3)	Al(2)−N(12)−C(13)	142.0(4)
N(9)−Al(2)−C(20)	117.5(3)	C(10)−N(12)−C(13)	123.0(5)
N(12)−Al(2)−C(19)	114.6(3)		

Results and Discussion

Synthesis and Characterization of (Me_2M)[NC_5H_4-CMeNNC(S)NR](MMe_2) (M = Al, Ga; R = CH_3, $^iC_3H_7$, C_6H_5) Prepared via the Methane Elimination Reaction. The reaction of 2-acetylpyridine 4-alkylthiosemicarbazone with trimethylaluminum or gallium in toluene at 35 °C affords the corresponding organoaluminum or gallium complexes, in which two hydrogen atoms have been lost from the aza hydrogen atoms via the methane elimination reaction (eq 1). The resulting yellow compounds **1**−**6** were isolated as air-sensitive crystalline solids in a nearly quantitative yield. These complexes are virtually insoluble in hexane but soluble in benzene, toluene, and THF. The complexes **1**−**6** have

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

Ga(1)−N(2)	2.033(3)	Ga(2)−C(13)	1.940(6)
Ga(1)−S(1)	2.378(1)	S(1)−C(9)	1.747(5)
Ga(1)−C(10)	1.953(6)	N(1)−N(2)	1.401(5)
Ga(1)−C(11)	1.961(7)	N(1)−C(7)	1.281(6)
Ga(2)−N(1)	2.070(3)	N(2)−C(9)	1.363(6)
Ga(2)−N(3)	1.996(4)	N(3)−C(9)	1.318(5)
Ga(2)−C(12)	1.965(6)	N(3)−C(14)	1.421(6)
S(1)−Ga(1)−N(2)	70.3(1)	C(12)−Ga(2)−C(13)	129.9(3)
S(1)−Ga(1)−C(10)	113.4(2)	Ga(1)−S(1)−C(9)	78.6(2)
S(1)−Ga(1)−C(11)	113.4(2)	Ga(2)−N(1)−N(2)	111.2(3)
N(2)−Ga(1)−C(10)	115.9(2)	Ga(2)−N(1)−C(7)	128.3(3)
N(2)−Ga(1)−C(11)	110.7(2)	N(2)−N(1)−C(7)	119.8(3)
C(10)−Ga(1)−C(11)	122.0(3)	Ga(1)−N(2)−N(1)	145.5(3)
N(1)−Ga(2)−N(3)	79.8(1)	Ga(1)−N(2)−C(9)	101.1(3)
N(1)−Ga(2)−C(12)	109.2(2)	N(1)−N(2)−C(9)	113.3(3)
N(1)−Ga(2)−C(13)	107.8(2)	Ga(2)−N(3)−C(9)	112.6(3)
N(3)−Ga(2)−C(12)	105.2(2)	Ga(2)−N(3)−C(14)	121.8(3)
N(3)−Ga(2)−C(13)	113.7(2)	C(9)−N(3)−C(14)	124.9(4)

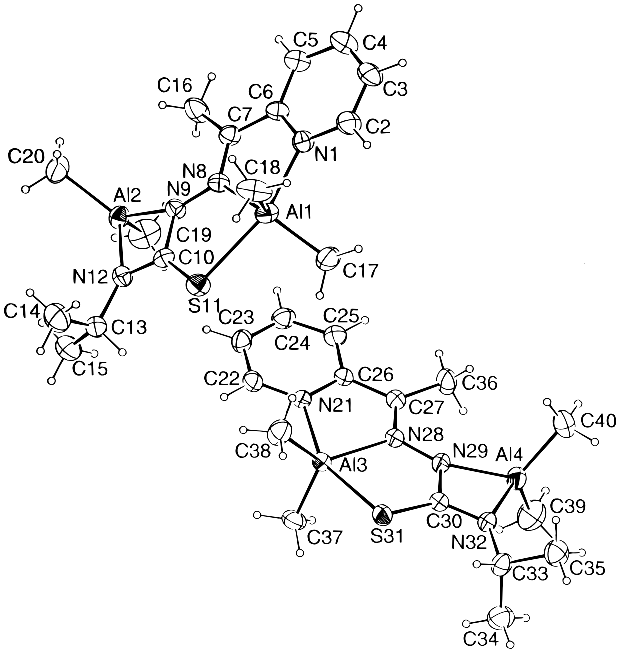
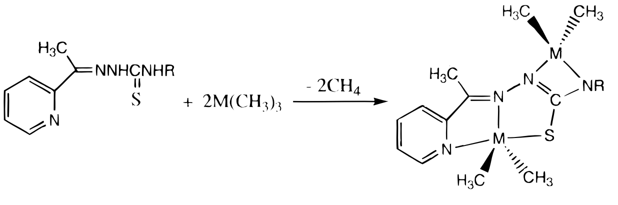


Figure 1. Molecular structure of (Me$_2$Al)[NC$_5$H$_4$CMeNNC(S)NC$_3$H$_7$](AlMe$_2$) (**3**). The thermal ellipsoids are drawn at the 50% probability level.



(1)

$\underline{1}$ M = Al, R = CH$_3$
$\underline{2}$ M = Ga, R = CH$_3$
$\underline{3}$ M = Al, R = ^{i}C$_3$H$_7$
$\underline{4}$ M = Ga, R = ^{i}C$_3$H$_7$
$\underline{5}$ M = Al, R = C$_6$H$_5$
$\underline{6}$ M = Ga, R = C$_6$H$_5$

been characterized by ^{1}H, ^{13}C, and ^{27}Al NMR, IR, and elemental analyses. The structure of compound **3** was determined based on its X-ray crystal structure. The ^{27}Al spectrum of **3** shows two distinct peaks at 152 ($w_{1/2}$ = 3764 Hz) and 114 ($w_{1/2}$ = 2672 Hz) ppm. The 152 ppm peak is characteristic of a four-coordinate Al atom, when compared with the shift of the four-coordinate Al atom in complexes of [R$_2$AlR′]$_2$ (R = Me, Et; R′ = NEt$_2$, OMe$_2$, OEt$_2$, etc.)[12] and [Al(CH$_3$C(CH$_2$NH)$_3$)$_2$(Al(CH$_3$)$_2$)$_3$].[13] The 114 ppm resonance is assigned to the five-coordinate Al(1). This value is within the range observed for five-coordinate Al atoms.[14] The ^{1}H NMR spectrum of **3** shows two peaks at −0.05 and −0.22 ppm due to the hydrogen atoms of the Al−Me groups. The chemical shifts of these two kinds of Al−Me groups are consistent with prior observations of five- and four-coordinate Al atoms.[10a,15] The finding that the peak of Al−Me in a N$_2$S coordination environment appears at higher field compared with that of Al−Me in a N$_2$ environment is consistent with the expected greater shielding of H on the Al−CH$_3$ group, as the two N, one S, and two C atoms provide a more electron-rich environment to Al(1) than that of Al(2), which is bonded to two N and two C atoms. The ^{13}C NMR spectrum of **3** also shows two peaks at −0.04 and −8.76 ppm due to the carbon atoms of the Al−CH$_3$ group in five- and four-coordinate environments. The carbons (C(8), C(6)) attached to the imine groups appear at 185.85 and 148.23 ppm in the ^{13}C NMR spectrum. The infrared spectrum of **3** indicates the mode of the ligand coordination to the aluminum moiety. The peak at 1590 cm^{-1} is assigned to the ring deformation mode. A positive shift in the mode compared to that of the ligand indicates that the pyridyl nitrogen coordinates in the complex. The stretching mode of ν(CS) at 775 cm^{-1} is significantly decreased. This could involve a tautomerism for the semicarbazone-3-thiol, i.e., a 1,3-proton shift (I−II).

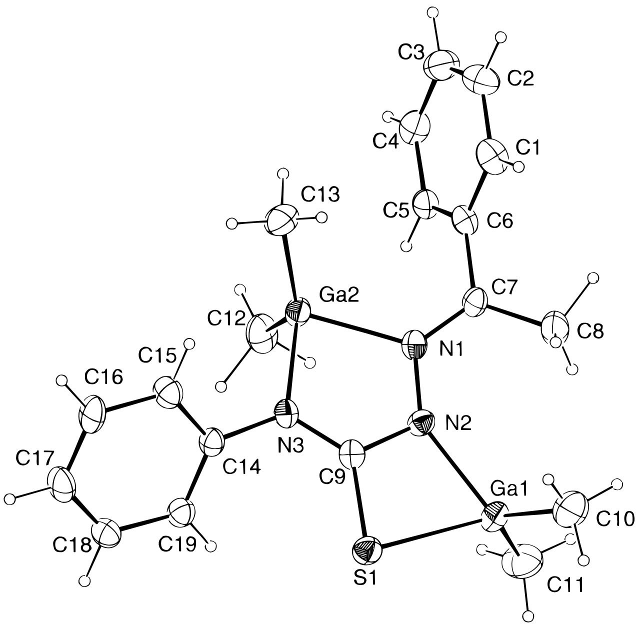


Figure 2. Molecular structure of (Me$_2$Ga)[PhMeCNNC(S)NPh](GaMe$_2$) (**8**). The thermal ellipsoids are drawn at the 30% probability level.

Synthesis and Characterization of (Me$_2$M)[RMeCNNC(S)NR′](MMe$_2$) (M = Al, Ga; R = CH$_3$, C$_6$H$_5$; R′ = CH$_3$, C$_6$H$_5$). The acetophenone thiosemicarbazone complexes of trimethylaluminum and gallium were synthesized using relatively straightforward reactions with toluene as the reaction solvent (eq 2). The complexes **7**−**10** are yellow crystalline solids at room

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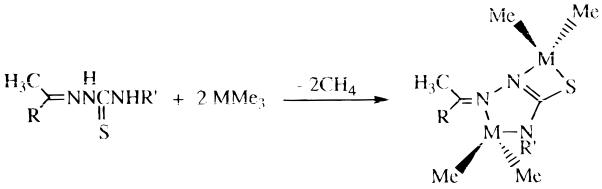

(2)

7 M = Al, R = C_6H_5, R' = C_6H_5
8 M = Ga, R = C_6H_5, R' = C_6H_5
9 M = Al, R = CH_3, R' = CH_3
10 M = Ga, R = CH_3, R' = CH_3

temperature, which are soluble in benzene, toluene, and THF. The initial indication of a dinuclear formulation for **8** stemmed from the observation of a parent ion in the mass spectrum at *m/z* 467, followed by a series of fragmentations attributable to the loss of Me groups. The dinuclear nature of the proposed structure was indicated by the ^1H and ^{13}C NMR spectral equivalence of the $GaMe_2$ moieties. Both the ^1H and ^{13}C NMR spectra of **8** exhibited two $Ga-CH_3$ resonances due to the methyl groups on the Ga(1) and Ga(2) atoms. Confirmation of the dinuclear structure of **8** was provided by X-ray crystallography.

Description of the Molecular Structure of (Me_2-Al)[$NC_5H_4C(CH_3)NNC(S)NC_3H_7$]($AlMe_2$) (3). Crystals of **3** suitable for an X-ray diffraction study were grown from toluene at −15 °C, and the structure of **3** was determined from data collected at −120 °C. A summary of the data collection and crystallographic parameters are given in Table 1. Selected bond lengths and angles are given in Table 2. An ORTEP diagram of the solid state structure giving the atom-numbering scheme used in the tables is shown in Figure 1.

The single-crystal structure of compound **3** indicates an asymmetric unit containing two unique molecules, which reside in general positions. The two molecules are almost identical in conformation and absolute configuration, but differ slightly in bond distances and angles. No symmetric element can be found in these structures. Coordinates for three carbon atoms with very high thermal motions are present. These three peaks lie near an inversion center and represent a poorly behaving hexane molecule. Al(1) and Al(3) are each included in both the AlN_2C_2 and AlN_2CS five-membered rings, while Al(2) and Al(4) are part of the AlN_2C four-membered ring.

Several points are worthy of note regarding the structure and bonding in **3**. Compound **3** contains two types of organoaluminum moieties with different coordination environments. The aluminum atom, Al(2), of the dimethylaluminum unit is found in the usual four-coordinate tetrahedral coordination geometry. However, the aluminum atom, Al(1), is clearly five-coordinate. Atoms N(8), Al(1), C(17), and C(18) constitute a basal plane, while the coordination sphere of Al(1) is completed by N(1) and S(11) residing in the axial positions on either side of the $N-Al-C_2$ basal plane. As the S(11)−Al(1)−N(1) bond angle is 156.5(2)° and the sum of the bond angles surrounding the Al atom on the basal plane is 360.0°, the coordination environment about Al(1) may be described as distorted trigonal bipyramidal (tbp). The distortion is mainly caused by the rigid geometry of the 2-acetylpyridine thiosemicarbazone ligand (bite angle, i.e., N(1)−Al(1)−N(8) 76.4(2)°; N(8)−Al(1)−S(11) 80.1(2)°), which prevents them from occupying exact tbp positions. The distorted geometry was found in other structural reports of the neutral five-coordinate organoaluminum complexes.[16] The Al(1)−S(11) distance (2.491(3) Å) is comparable to that observed for $K[Al_2(CH_3)_6SCN]$ (2.489(2) Å)[17] and $[Al(CH_3)_3]_4[14]aneS_4$ (2.522(2) Å).[18] The pyridyl Al(1)−N(1) distance (2.076(5) Å) is slightly longer than the amido Al(1)−N(8) distance (2.040(5) Å), a feature consistent with the literature.[19] The Al(1)−C(17) bond distance (1.962(7) Å) falls well within the range commonly found for five-coordinate aluminum complexes.[14,16] The other Al(2) atom is in the AlN_2C units. The geometry about the aluminum atom, Al(2), can be described as a distorted tetrahedron. The N(9)−Al(2)−N(12) angle is extremely restricted by the N_2C ring, 67.7(2)°. However, the C(19)−Al(2)−C(20) angle trans to it is 118.0(3)°. The methyl ligands are rotated away from the nitrogen donor atoms, giving an average C−Al−N angle of 115.2(3)°. The imine N(9)−Al(2) bond distance (1.946(5) Å) is longer than the amido N(12)−Al(2) distance (1.915(5) Å), indicating that the negatively charged amido nitrogen atom is a stronger donor to the aluminum center than the neutral imine nitrogen atom. The proximity of the amido nitrogen atom to the aluminum atom appears to be the reason for the asymmetric arrangement.

Molecular Structure Desorption of (Me_2Ga)-[PhMeCNNC(S)NPh]($GaMe_2$) (8). A crystal of **8** suitable for X-ray diffraction study was grown from toluene at −15 °C. A summary of the data collection and crystallographic parameters for **8** is given in Table 1. The relevant bond lengths and angles are shown in Table 3. The molecular structure of **8** is given in Figure 2. The molecule contains one GaN_2C_2 five-membered ring and one GaCNS four-membered ring. In the solid state, the Ga(1) center is coordinated by two nitrogen atoms and two methyl groups in a distorted tetrahedral configuration. The imine N(1)−Ga(2) distance (2.070(3) Å) is slightly longer than the amido N(3)−Ga(2) distance (1.996(4) Å). Significant distortion from an ideal tetrahedral geometry is observed for the gallium atom, Ga(1), in the constrained four-membered ring; the ring angle at aluminum is 70.3(1)°. The Ga(1)−S(1) bond distance (2.378(1) Å) is slightly longer than that observed for $[py(^tBu)GaS]_3$ (2.231(3)−2.253(3) Å)[20] and for the thiolate-bridged complexes $Ga_4I_4(SME)_4S_2$ (2.204(8) Å).[21] However, the Ga(1)−S(1) and Ga(1)−N(2) (2.033(3) Å) bond distances in **8** are comparable to those of the pyridine-2-thiol complex $Ga_2(OEt)_2(2\text{-}C_5H_4NS)_4$ (Ga−S = 2.431(2) Å; Ga−N = 2.100(4) Å) and $Ga(SC_5H_4N)_3$ (Ga−S = 2.420(3) Å; Ga−N = 2.062(8) Å).[22] The relatively long Ga(1)−S(1) and Ga(1)−N(2) bond

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distances in **8** is primarily the result of ring strain due to the endocyclic bond angle of 70.3(1)°.

Summary

The ten new complexes described here significantly expand upon the few examples of well-characterized aluminum and gallium complexes of *N*-heterocyclic carboxaldehyde thiosemicarbazones. A combination of X-ray crystallographic and spectroscopic studies confirms the nature of these compounds. The X-ray crystallographic study of $(Me_2Al)[NC_5H_4C(CH_3)NNC(S)NC_3H_7](AlMe_2)$ (**3**), described above, provides the first structural data for the dinuclear aluminum nature with a five-coordinate AlN_2SC_2 and a four-coordinate AlN_2C_2 environment. The terdentate acetylpyridine thiosemicarbazones, which have a thiol group, are valuable for the synthesis of new polynuclear alkylaluminum and -gallium complexes with different coordination environments. In addition, modification of the organic substituents on these ligands should allow tuning of their steric bulk and, as a result, the derivative of the product compounds. These ligands also display complicated bonding modes which require further investigation in order to be understood.

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Supporting Information Available: Text describing the X-ray structure determination, tables of structure determination details, bond distances and angles, atomic coordinates, and thermal parameters, and ORTEP diagrams for compounds **3** and **8** (34 pages). Ordering information is given on any current masthead page.

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