Synthesis and Characterization of New Trinuclear Aluminum and Gallium Complexes of Bis(thiosemicarbazones). Single-Crystal Structure of (MeAl)$\{CH_2[C(Me)NNC(S)N(Me)]_2\}(AlMe_2)_2$

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*Summary: Novel trinuclear metal complexes of formula (MeM)$\{CH_2[C(CH_3)NNC(S)(NR)]_2\}(MMe_2)_2$ (M = Al, R = Me (**1**); M = Ga, R = Me (**2**); M = Al, R = Et (**3**): M = Ga, R = Et (**4**); M = Al, R = Ph (**5**); M = Ga, R = Ph (**6**)) result when the ligands 2,4-bis(4-N-alkylthiosemicarbazono)pentane are mixed with trimethylaluminum and -gallium reagents and were characterized by ^1H, ^{13}C, and ^{27}Al NMR, mass spectra, and elemental analyses. The structure of the compound **1** has been determined by single-crystal X-ray diffraction analysis. The structural data reveal that compound **1** is a trinuclear aluminum compound with coordination numbers of 4 and 5.*

Introduction

α-N-heterocyclic carboxaldehyde thiosemicarbazones and bis(thiosemicarbazones) comprise two interesting classes of experimental cancer chemotherapeutic agents in that both are strong metal chelating agents.[1] Extensive literature on the antitumor properties of metal complexes of heterocyclic carboxaldehyde thiosemicarbazones is now available.[2] In particular, gallium(III) complexes of heterocyclic carboxaldehyde thiosemicarbazones continue to attract attention due to the fact that ^{67}Ga, a low-energy γ-emitting radionuclide,[3] is a very useful tumor diagnostic agent. Kepper and co-workers[4] developed gallium complexes employing the ligands which themselves had antiviral and antitumor activity. We[5] have recently prepared a series of dinuclear group 13 heterocyclic carboxaldehyde thiosemicarbazone complexes $(Me_2M)[NC_5H_4CMeNNC(S)NR](MMe_2)$ (M = Al, Ga; R = Me, $^iC_3H_7$, Ph). However, the coordination chemistry of bis(thiosemicarbazone) ligands with aluminum and gallium remains unexplored. We have decided to investigate the coordination ability of bis(thiosemicarbazones), which contain two semicarbazones with two thiol groups (Chart 1) or alternatively two donor entities HNC═S (Chart 1) that should be useful for the construction of polynuclear complexes. Since the general type of reaction, namely evolution of alkane from interaction of AlR_3/GaR_3 with N−H/S−H bonds, is well established for open chain systems,[6] it is useful to investigate the preparation and structural properties of alkyl complexes of group 13 organometallic derivatives of bis(thiosemicarbazones). We report here the synthesis and characterization of several bis(thiosemicarbazone) complexes (MeM)$\{CH_2[C(CH_3)NNC(S)(NR)]_2\}(MMe_2)_2$ (M = Al, Ga; R = Me, Et, Ph) and the single-crystal X-ray structure of one of these.

Experimental Section

General Procedures. Standard inert-atmosphere techniques were used for the synthesis and manipulation of all compounds owing to their air and moisture sensitivity. This included the use of a high-vacuum line in conjunction with an inert-atmosphere drybox. Toluene and hexane were distilled under an atmosphere of nitrogen from sodium/benzophenone. $AlMe_3$ and $GaMe_3$ were purchased from Strem Chemicals. Benzene-d_6 was purchased from Aldrich and stored over molecular sieves. The bis(thiosemicarbazones) of pentane-2,4-dione were prepared by the literature method.[14]

^1H, ^{13}C, and ^{27}Al NMR spectral data were recorded on a Bruker WH-300 spectrometer. The ^1H and ^{13}C chemical shifts are referenced relative to benzene-d_6 (^1H, δ 7.16; $^{13}C\{^1H\}$, δ

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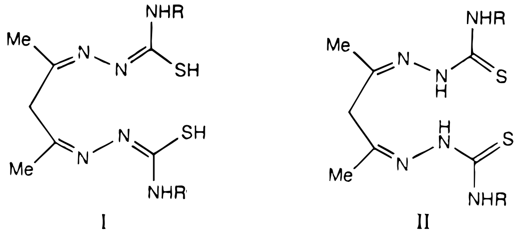
Chart 1



128.00), while aqueous Al(NO$_3$)$_3$ is used as the ^{27}Al external reference. IR data were collected using a Shimadzu FT-IR 8501 spectrometer. Mass spectra were recorded on a high-resolution VG70-VSEG mass spectrometer. Elemental analyses were performed by the Basic Science Center, Seoul, Korea.

General Synthesis of $[(CH_3)M]\{CH_2[C(CH_3)NNC(\_S)(NR)]_2\}[\_M(CH_3)_2]_2$. In a typical synthesis, trimethylaluminum or gallium (6 mmol) in toluene (10 mL) was added dropwise to a stirred suspension of bis(thiosemicarbazone) of pentane-2,4-dione (2 mmol) in toluene (10 mL) at room temperature and the reaction mixture turned yellow immediately. Slow warming of the mixture to 50 °C resulted in significant gas evolution. The mixture was stirred for 2 h at that temperature unitl no further gas evolution was observed, and then the solvent was reduced to ca. 10 mL. A 3 mL volume of hexane was layered on this solution. The solution was set aside in the freezer (0 °C) for 2 days to give colorless crystals in 80−90% yield.

(MeAl)$\{CH_2[C(CH_3)NNC(S)(NMe)]_2\}(AlMe_2)_2$ (1). Mp: 229−233 °C. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 4.06 (d, J = 13.22 Hz, 1 H, CH), 2.75 (s, 6H, NCH_3), 1.66 (d, J = 13.22 Hz, 1H, CH), 1.38 (s, 6H, CCH_3), 0.19 (s, 3H, $AlCH_3$), −0.66 (s, 12H, $AlCH_3$). $^{13}C\{^1H\}$ NMR (C$_6$D$_6$, 25 °C): δ 182.65 (CS), 149.43 (CN), 38.01 (CH_2), 33.06 (NCH_3), 22.99 (CCH_3), −0.04 ($AlCH_3$), −10.71 ($AlCH_3$). ^{27}Al NMR: δ 162, 92. IR (on KBr pellet; cm^{-1}): 2885 (br), 2852 (w), 1525 (br, s), 1500 (br, s), 1421 (w), 1386 (m), 1366 (w), 1334 (w), 1305 (w), 1287 (br, m), 1260 (w), 1254 (w), 1218 (w), 1178 (m), 1145 (w), 1115 (br, s), 1080 (br, w), 1035 (w), 1025 (w), 971 (w), 956 (w), 909 (w), 863 (w), 850 (br, w), 835 (br, w), 773 (m), 730 (w), 705 (m). MS (EI): m/z 426 [M$^+$], 411 [M$^+$ − CH$_3$]. Anal. Calcd for $C_{14}H_{29}N_6S_2Al_3$: C, 39.43; H, 6.85. Found: C, 39.08; H, 6.62.

(MeGa)$\{CH_2[C(CH_3)NNC(S)(NMe)]_2\}(GaMe_2)_2$ (2). Mp: 150 °C. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 3.92 (d, J = 12.88 Hz, 1H, CH), 2.86 (s, 6H, NCH_3), 1.75 (d, J = 12.88 Hz, 1H, CH), 1.45 (s, 6H, CCH_3), 0.52 (s, 3H, $GaCH_3$), −0.18 (s, 6H, $GaCH_3$), −0.31 (s, 6H, $GaCH_3$). $^{13}C\{^1H\}$ NMR (C$_6$D$_6$, 25 °C): δ 180.69 (CS), 145.85 (CN), 37.13 (CH_2), 32.84 (NCH_3), 23.22 (CCH_3), −0.04 ($GaCH_3$), −6.99 ($GaCH_3$). IR (on KBr pellet; cm^{-1}): 2890 (br, s), 2835 (m), 1525 (s), 1510 (br, s), 1485 (sh), 1424 (w), 1386 (s), 1369 (s), 1295 (br, s), 1279 (w), 1255 (br, s), 1235 (w), 1193 (m), 1187 (w), 1171 (w), 1110 (s), 1035 (w), 1044 (w), 1016 (w), 1000 (w), 911 (w), 863 (w), 852 (w), 843 (br, w), 805 (w), 789 (m), 850 (w), 730 (w), 716 (m), 695 (w), 665 (w), 648 (w), 619 (m). MS(EI): m/z 554 [M$^+$], 539 [M$^+$ − CH$_3$]. Anal. Calcd for $C_{14}H_{29}N_6S_2Ga_3$: C, 30.31; H, 5.27. Found: C, 30.44; H, 5.40.

(MeAl)$\{CH_2[C(CH_3)NNC(S)(NEt)]_2\}(AlMe_2)_2$ (3). Mp: 200 °C (dec). ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 4.52 (d, J = 12.74 Hz, 1H, CH), 3.46 (q, J = 7.34 Hz, 4H, CH_2CH_3), 2.97 (d, J = 12.74 Hz, 1H, CH), 2.32 (s, 6H, CCH_3), 1.28 (t, J = 7.34 Hz, 6H, CH_2CH_3), −0.25 (s, 3H, $AlCH_3$), −0.63 (s, 12H, $AlCH_3$). $^{13}C\{^1H\}$ NMR (C$_6$D$_6$, 25 °C): δ 183.69 (CS), 153.09 (CN), 38.93 (CH_2), 31.90 (NCH_3), 23.42 (CCH_3), 14.62 (CH_2CH_3), −2.74 ($AlCH_3$), −3.17 ($AlCH_3$). ^{27}Al NMR: δ 160, 88. IR (on KBr pellet; cm^{-1}): 2965 (w), 2919 (w), 1543 (w), 1519 (sh), 1505 (s), 1485 (sh), 1442 (br, w), 1430 (w), 1385 (w), 1350 (w), 1344 (w), 1324 (w), 1305 (br, w), 1276 (w), 1260 (w), 1246 (w), 1234 (w), 1225 (w), 1211 (w), 1190 (w), 1163 (w), 1130 (m), 1100 (w), 1050 (br, w), 1025 (w), 895 (w), 850 (br, w), 800 (w), 773 (w), 728 (w), 695 (w). Anal. Calcd for $C_{16}H_{33}N_6S_2Al_3$: C, 42.28; H, 7.27. Found: C, 41.94; H, 7.03.

(MeGa)$\{CH_2[C(CH_3)NNC(S)(NEt)]_2\}(GaMe_2)_2$ (4). Mp: 102−105 °C. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 3.93 (d, J = 12.62 Hz, 1H, CH), 3.41 (q, J = 7.28 Hz, 4H, CH_2CH_3), 1.71 (d, J = 12.62 Hz, 1H, CH), 1.40 (s, 6H, CCH_3), 0.97 (t, J = 7.28 Hz, 6H, CH_2CH_3), 0.62 (s, 3H, $GaCH_3$), −0.12 (s, 6H, $GaCH_3$), −0.27 (s, 6H, $GaCH_3$). $^{13}C\{^1H\}$ NMR (C$_6$D$_6$, 25 °C): δ 183.48 (CS), 152.87 (CN), 39.05 (CH_2), 25.76 (CCH_3), 14.27 (CH_2CH_3), −2.12 ($GaCH_3$), −4.02 ($GaCH_3$), 4.39 ($GaCH_3$). IR (on KBr pellet; cm^{-1}): 2953 (w), 1600 (w), 1535 (w), 1490 (w), 1470 (w), 1458 (w), 1438 (w), 1383 (w), 1327 (w), 1295 (br, w), 1264 (w), 1207 (w), 1186 (w), 1173 (w), 1145 (w), 1123 (w), 1071 (w), 1020 (w), 950 (w), 904 (w), 862 (w), 855 (w), 810 (m), 750 (m), 725 (w), 661 (w). Anal. Calcd for $C_{16}H_{33}N_6S_2Ga_3$: C, 32.98; H, 5.67. Found: C, 32.61; H, 5.44.

(MeAl)$\{CH_2[C(CH_3)NNC(S)(NC_6H_5)]_2\}(AlMe_2)_2$ (5). Mp: 163−165 °C. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 7.29−7.32 (m, 4H, *Ph*), 7.06−7.11 (m, 4H, *Ph*), 6.93−6.95 (m, 2H, *Ph*), 4.25 (d, J = 12.92 Hz, 1H, CH), 1.75 (d, J = 12.92 Hz, 1H, CH), 1.44 (s, 6H, CCH_3), 0.22 (s, 3H, $AlCH_3$), −0.40 (s, 6H, $AlCH_3$), −0.53 (s, 6H, $AlCH_3$). $^{13}C\{^1H\}$ NMR (C$_6$D$_6$, 25 °C): δ 178.04 (CS), 148.24 (CN), 142.74, 138.09, 137.84, 121.97, 120.22, 35.32(CH_2), 22.48 (CCH_3), −1.54 ($AlCH_3$), −8.47 ($AlCH_3$). IR (on KBr pellet; cm^{-1}): 3040 (w), 2930 (w), 1583 (m), 1510 (w), 1500 (br, s), 1480 (sh), 1436 (w), 1397 (w), 1350 (br), 1310 (w), 1300 (w), 1252 (w), 1200 (w), 1180 (w), 1123 (w), 1020 (br), 997 (w), 984 (w), 848 (w), 748 (w), 690 (w). Anal. Calcd for $C_{24}H_{33}N_6S_2Al_3$: C, 52.37; H, 6.00. Found: C, 51.98; H, 5.84.

(MeGa)$\{CH_2[C(CH_3)NNC(S)(NC_6H_5)]_2\}(GaMe_2)_2$ (6). Mp: 180 °C (dec). ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 7.32−7.36 (m, 4H, *Ph*), 7.07−7.12 (m, 4H, *Ph*), 6.90 (m, 2H, *Ph*), 4.06 (d, J = 12.76 Hz, 1H, CH), 1.70 (d, J = 12.76 Hz, 1H, CH), 1.37 (s, 6H, CCH_3), 0.39 (s, 3H, $GaCH_3$), −0.06 (s, 6H, $GaCH_3$), −0.28 (s, 6H, $GaCH_3$). IR (on KBr pellet; cm^{-1}): 3030 (w), 3015 (w), 2960 (w), 2900 (w), 1590 (m), 1488 (s), 1460 (s), 1440 (sh), 1380 (m), 1322 (w), 1310 (m), 1300 (w), 1281 (w), 1258 (m), 1240 (s), 1107 (w), 1072 (w), 1053 (w), 1030 (w), 1002 (w), 986 (w), 965 (m), 918 (w), 886 (w), 845 (w), 756 (m), 730 (w), 700 (w), 691 (w), 655 (w), 643 (m). MS(EI): m/z 678 [M$^+$], 663 [M$^+$ − CH$_3$], 454 [M$^+$ − GaCH$_3$]. Anal. Calcd for $C_{24}H_{33}N_6S_2Ga_3$: C, 42.46; H, 4.87. Found: C, 42.18; H, 4.62.

X-ray Structural Analysis of Complex 1. Data were collected on a Rigaku/RAXIS IIc area detector by employing graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) at a temperature of 228 K. Indexing was performed from a series of 1° oscillation images with exposures of 5 min/frame. A total of 9353 reflections were measured over the following ranges: $0.0 \le 2\theta \le 49.9°$, $-29 \le h \le 29$, $0 \le k \le 8$, $-15 \le l \le 15$. Of the reflections measured a total of 974 unique reflections with $F^2 > 3.0\sigma(F^2)$ were used during subsequent structure refinement.

The structure was solved by direct methods. Refinement was 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 refined anisotropically, and hydrogen atoms were included as constant contributions to the structure factors and were not refined. Refinement converged to $R1$ = 0.0333 and $R2$ = 0.0401. Crystallographic data are given in Table 1, and selected bond distances and angles for **1** are given in Table 2. The molecular structure of compound **1** is given in Figure 1.

Results and Discussion

Synthesis and Characterization of Trimeric Aluminum and Gallium Complexes of Bis(thiosemicarbazone). The reaction of bis(thiosemicarbazones) of pentane-2,4-dione with trimethylaluminum or gallium in toluene at 50 °C affords the corresponding trimeric organoaluminum and gallium complexes, in

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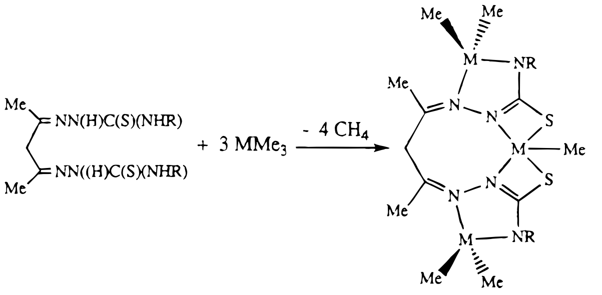
Table 1. Crystallographic Data for the Structural Studies of Compound 1

empirical formula	$C_{14}H_{29}N_6S_2Al_3$
fw	426.29
cryst system	orthorhombic
space group	$Cmc2_1$
cell constant	
a, Å	24.956(3)
b, Å	7.1212(8)
c, Å	12.744(2)
V, Å^3	2264.8(4)
Z	4
D_{calcd}, g cm^{-3}	1.251
$F(000)$	118
μ(Mo Kα), λ	0.710 69 Å
no. of indep reflcns	1158
params refined	974
goodness of fit	1.80
$R1^a$	0.0333
w$R2^a$	0.0401

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; w$R2 = \{\sum[w(F_o^2 - F_c^2)^2[/\sum[wF_o^2]]\}^{1/2}$.

which four hydrogen atoms have been lost from the aza hydrogen atoms via the methane elimination reaction according to eq 1. The resulting yellow products **1**−**6**



(1)

R = Me , M = Al (**1**) ; R = Me , M = Ga (**2**)
R = Et , M = Al (**3**) ; R = Et , M = Ga (**4**)
R = Ph , M = Al (**5**) ; R = Ph , M = Ga (**6**)

were isolated as moderately air-sensitive, crystalline solids in high yield. These compounds are readily soluble in benzene, toluene, and THF. Compounds **1**−**6** were characterized by ^{1}H, ^{13}C, and ^{27}Al NMR, mass spectrometry, and elemental analysis. The structure of compound **1** was determined by single-crystal X-ray diffraction. The initial indication of the trinuclear formulation for **1** stemmed from the observation of a parent ion in the mass spectrum at m/z 426, followed by a series of fragmentations attributable to the loss of Me groups. The mass spectral data for **2**, **4**, and **6** were consistent with the trinuclear formulation. NMR spectroscopic data for **1** are consistent with the solid-state structure as determined by X-ray crystallography. The ^{27}Al NMR spectrum of **1** at room temperature consists of two distinct resonances at 162 and 92 ppm. The 162 ppm resonance 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.).[7] The 92 ppm resonance is assigned to the five-coordinate Al(1). The value is comparable to that observed for five-coordinate Al atoms.[8] In the ^{1}H NMR spectrum of **1**, the methyl groups of the aluminum moieties give rise to two signals at δ 0.19 and −0.66 in the region expected for a σ-bonded species due to the hydrogen atoms of the Al−Me groups; the CH$_2$ protons give rise to two doublet resonances at δ 4.06 and 1.66 and the CCH$_3$ and NCH$_3$ protons give rise to two distinct peaks at 1.38 and 2.75 ppm, respectively, due to the mirror plane. The chemical shifts of these two kinds of Al−CH$_3$ are consistent with prior observation of five- and four-coordinate Al atoms.[9] The finding that the resonance of Al−Me in a N$_2$S$_2$ 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, two S, and one C atoms provide a more electron-rich environment for Al(1) than those for Al(2) and Al(2*), which are bonded to the two N and two C atoms. Similarly, the ^{13}C NMR spectrum of **1** shows two resonances at δ −0.04 and −10.71 ppm which are due to the carbon atoms of the Al−CH$_3$ group in five- and four-coordinate environments, respectively. The carbons (C(5) and C(5*), C(2) and C(2*)) attached to the imine groups appear at δ 182.65 and 149.43. The ^{1}H and ^{13}C NMR spectra of the other complexes are well in agreement with those of the trimeric nuclear product **1**. In the infrared spectrum of **1**, the stretching mode ν(CS) at 773 cm^{-1} is significantly decreased. This could involve a tautomerism for semicarbazone-3-thiol, i.e., a 1,3-proton shift (I ↔ II). Although all the spectra are consistent with the proposed formulation, the bonding mode in **1** is still unclear. Accordingly, the trimeric nature and the coordination geometries of the metal centers for **1** were confirmed through single-crystal X-ray diffraction analysis.

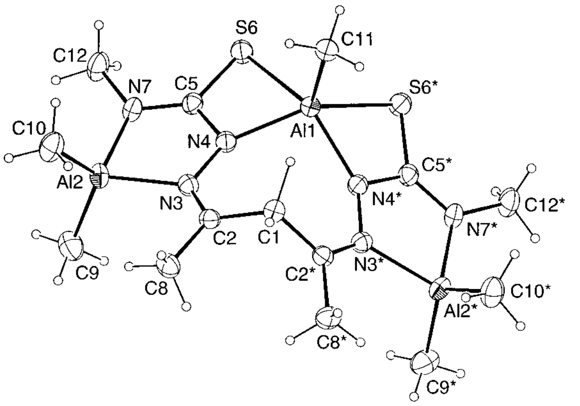


Figure 1. Molecular structure of (MeAl){CH$_2$[C(CMe)NNC(S)NMe]$_2$}(AlMe$_2$)$_2$ (**1**). The thermal ellipsoids are drawn at the 30% probability level.

Description of the Molecular Structure of 1. Details of the X-ray data collection and structure refinement for compound **1** are presented in Table 1. 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, the molecule of **1** possesses a mirror plane on which the Al(1), C(11), and C(1) atoms lie. Furthermore, the molecule consists of a series of two four-membered AlNCS rings and two five-membered AlN$_3$C rings.

Of paramount significance is the coordination of the aluminum atoms in (MeAl){CH$_2$[C(CH$_3$)NNC(S)(NMe)]$_2$}(AlMe$_2$)$_2$. Compound **1** contains two types of dimethylaluminum fragment. Two aluminum atoms, Al(2) and

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

S(6)−Al(1)	2.414(1)	S(6)−C(5)	1.720(4)	Al(1)−N(4)	1.967(3)
Al(1)−N(4)	1.967(3)	Al(1)−C(11)	1.936(6)	Al(2)−N(3)	2.001(3)
Al(2)−N(7)	1.897(4)	Al(2)−C(9)	1.936(5)	Al(2)−C(10)	1.944(5)
N(3)−N(4)	1.394(4)	N(3)−C(2)	1.287(5)	N(4)−C(5)	1.364(5)
N(7)−C(5)	1.307(5)	N(7)−C(12)	1.465(6)	C(1)−C(2)	1.499(5)
C(1)−C(2)	1.499(5)	C(2)−C(8)	1.483(6)		

Al(1)−S(6)−C(5)	77.2(1)	S(6)−Al(1)−S(6*)	95.9(1)	S(6)−Al(1)−N(4)	69.7(1)
S(6)−Al(1)−N(4*)	141.1(1)	S(6)−Al(1)−C(11)	107.2(1)	N(4)−Al(1)−N(4*)	98.6(2)
N(4)−Al(1)−C(11)	111.5(2)	N(3)−Al(2)−N(7)	82.3(1)	N(3)−Al(2)−C(9)	112.2(2)
N(3)−Al(2)−C(10)	108.3(2)	N(7)−Al(2)−C(9)	112.8(2)	N(7)−Al(2)−C(10)	113.2(2)
C(9)−Al(2)−C(10)	121.2(2)	Al(2)−N(3)−N(4)	111.3(2)	Al(2)−N(3)−C(2)	127.2(3)
N(4)−N(3)−C(2)	120.8(3)	Al(1)−N(4)−N(3)	114.6(2)	Al(1)−N(4)−C(5)	103.1(2)
N(3)−N(4)−C(5)	111.9(3)	Al(2)−N(7)−C(5)	113.4(3)	Al(2)−N(7)−Cl(2)	127.2(3)
C(5)−N(7)−C(12)	119.4(3)	C(2)−C(1)−C(2)	116.8(5)	N(3)−C(2)−C(1)	122.9(4)
N(3)−C(2)−C(8)	118.6(4)	C(1)−C(2)−C(8)	118.4(4)	S(6)−C(5)−N(4)	109.7(3)
S(6)−C(5)−N(7)	129.2(3)	N(4)−C(5)−N(7)	121.1(3)		

Al(2*), have the usual four-coordinate tetrahedral organoaluminum coordination. However, the situation for the remaining aluminum atoms is quite different. An examination of Al(1) reveals it to be five-coordinate being bonded to an axially positioned methyl carbon, C(11), in addition to two amido nitrogen atoms and two thiolato atoms. The N(4)−Al(1)−S(6) angle is extremely restricted by the NCS ring to 69.7(1)°. As the N(4)−Al(1)−S(6*) and N(6)−Al(1)−C(11) bond angle are 141.1(1) and 107.2(1)°, respectively, the coordination environment about Al(1) may be described as square pyramidal. Such is completely unprecedented. The literature reveals many other structural reports of neutral five-coordinate organoaluminum complexes.[8,10] Of these complexes only a few have square pyramidal coordination,[6a,11] while the others have trigonal bipyramidal coordination. The Al(1)−N(4) distance in the square pyramid is 1.967(3) Å. The amido Al(1)−N(4) distance is slightly shorter than those of the pyridyl Al−N bond and other amido Al−N bond.[10a] The Al(1)−S(6) distance (2.414(1) Å) is comparable to that observed for Ga(SC$_5$H$_4$N)$_3$ (2.420(3) Å)[12] and [Ga$_2$(OC$_2$H$_5$)$_2$(SC$_5$H$_4$N)$_4$] (2.431(2) Å).[12] The Al(1)−C(11) bond distance (1.936(6) Å) is typical for five-coordinate aluminum complexes.[10] The other two atoms, Al(2) and Al(2*), can be described as a distorted tetrahedron. The C(9)−Al(2)−C(10) angle is 121.2(2)°. The methyl ligands are rotated away from nitrogen donor ligands, giving an average C−Al−N angle of 112.8(2)°. The imine Al(2)−N(3) bond distance (2.001(3) Å) is longer than the amido Al(2)−N(7) distance (1.897(4) Å), indicating that the negatively charged amido atom is a stronger donor to the aluminum center than the neutral imine atom. The proximity of the amido nitrogen atom to the aluminum atom appears to be the reason for the asymmetric arrangement. The imine N(4)−C(5) bond distance (1.346(5) Å) is shorter than that of the single bond distance of C−N (1.43 Å). The changes in bond distances for the thiocarbamide group [S(6)C(5)N(3)N(7)] indicate that metalation shifts the S(6)−C(5) toward its thiol form and bond multiplicity shifts from C(5)−N(7) toward C(5)−N(4), probably due to the displacement of the π charge.

The use of the bis(thiosemicarbazones) of pentane-2,4-dione as ligands in the organometallic chemistry of aluminum and gallium leads to a trimeric organometallic complexes of these metals having uncommon coordination geometries. X-ray crystallographic studies and spectroscopic parameters confirm that these complexes represent rather unusual four- and five-coordinate geometries. Our continuing investigations are oriented concerning factors which determined coordination geometries in five-coordinate organoaluminum and gallium complexes.

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Supporting Information Available: Text describing X-ray procedures and tables of bond distances and angles, atomic coordinates, fractional coordinates for the hydrogen atoms, thermal parameters, and X-ray data for compound **1** (8 pages). Ordering information is given on any current masthead page.

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