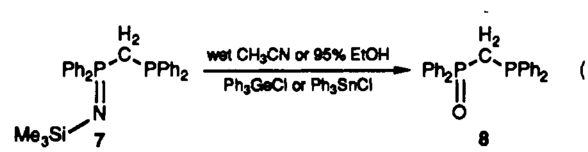

(1)

ethanol. Formation of **8** from the above reaction contrasts the formation of the diphosphazene **4** from **1** (Scheme I), and it is clear that the rearrangement involves a cooperative interaction of two iminophosphorane centers. This result in conjuction with our findings clearly establishes that the P–C–P links in dppm derivatives are more reactive than the phosphorus–aryl carbon bonds in such compounds. In contrast, phosphorus–aryl carbon bond scission reactions are observed for a number of tertiary phosphine–metal complexes.[3]

Several interesting features are provided by the structure of **4**. Most notable is the observation of a hydrogen-bonding interaction between the chloride and the amino hydrogens. This presumably accounts for the dimeric, centrosymmetric solid-state structure exhibited by **4**. The P–N bond lengths (1.57 Å) within the PNP segment are equivalent and are clearly characteristic of P–N double bonds. The long P–N bond (1.62 Å) for the protonated nitrogen also falls within the range for compounds with isolated P–N double bonds,[22-26] but the bond is shorter than the value expected for a single bond. Qualitatively the compound is clearly best formulated as an aminodiphosphinimine

$$H_2N{-}P(Ph_2){=}N^+{=}PPh_2Me$$

with each P doubly bonded to an imine nitrogen. The charge is probably best placed on the bridge nitrogen. The P=N=P angle is 142.9°. All of these structural features compared well with those of $Ph_3P{=}N{=}PPh_3^+$ (PN bond lengths (1.575 Å (average), P=N=P angle 136°)[25] and the backbone PN bonds of $(H_2N)Ph_2P{=}N{=}PPh_2(NH_2)^+$ (1.575 Å) (average), P=N=P angle 142°)[31]. The terminal NH_2 groups in the latter are similarly bonded to phosphorus ($P{-}NH_2$ = 1.65 Å (average))[26] as in the case of **4**.

Investigations into the chemistry of this interesting compound and into the influence of aryl- or alkylgermanium and tin halides on the hydrolysis pathways of transition-metal–phosphine complexes are underway.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for Financial support.

Supplementary Material Available: For **4**, text describing the structure solution, listings of X-ray details, bond distances, bond angles, positional and isotropic equivalent displacement parameters, general displacement (*U*) parameters, and ^{13}C NMR data, and figures showing alternative ORTEP views and a ^{13}C NMR spectrum (14 pages); a table of observed and calculated structure factors (16 pages). Ordering information is given on any current mesthead page.

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Synthesis and Characterization of the Neutral Three-Coordinate Thiolate Complexes $Al[S(2,4,6\text{-}t\text{-}Bu_3C_6H_2)]_3$ and $Ga[S(2,4,6\text{-}t\text{-}Bu_3C_6H_2)]_3$

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The first monomeric, three-coordinate aluminum and gallium thiolate compounds have been synthesized and structurally characterized. The compounds were prepared by the reaction of the corresponding metal halide with 2 equiv of LiSMes* (Mes* = $2,4,6\text{-}t\text{-}Bu_3C_6H_2$) to give the aluminum derivative $Al(SMes^*)_3$ (**1**) or with 3 equiv of the lithium thiolate to give the gallium species $Ga(SMes^*)_3$ (**2**). The compounds were characterized by ^1H NMR and infrared spectroscopy and X-ray crystallography. Crystal data with Mo Kα (λ = 0.71069 Å) radiation at 130 K: **1**, $Al(SMes^*)_3$, $C_{54}H_{87}AlS_3$, a = 10.229 (5) Å, b = 26.137 (7) Å, C = 19.908 (5) Å, β = 91.260 (3)°, Z = 4, monoclinic, space group $P2_1/n$, $R(F)$ = 0.049; **2**, $Ga(SMes^*)_3$, $C_{54}H_{87}GaS_3$, a = 10.243 (2) Å, b = 26.189 (8) Å, c = 20.031 (3) Å, β = 91.554 (1)°, Z = 4, monoclinic, space grup $P2_1/n$, $R(F)$ = 0.049. The structural data show that **1** and **2** have a very similar three-coordinate, almost planar, geometry at the metal. Distortions from idealized trigonal-planar coordination, as well as other structural features can be explained on the basis of ionic M–S bonding character and of some M···H interactions involving the *o*-*t*-Bu groups of the ligand.

Introduction

In spite of the large amount of research on the inorganic and organometallic chemistry of heavier main-group 3 (Al–Tl) complexes, relatively little is known about their compounds with low (3 or less) coordination numbers. For example, only a small number of such compounds have been structurally characterized in the solid state,[1-14] and most of these have been published within the last 5 years. In the case of Al and Ga derivatives, the compounds $Al[N(SiMe_3)_2]_3$,[1] $MMes_3$ (M = Al,[2] Ga[3]), $Ga(AsMes_2)_3$,[4] $Ga[P(H)Mes^*]_3$,[5] $(\eta^1\text{-}C_5Me_5)_2GaAs(SiMe_3)_2$,[6] $MeAl[O(2,6\text{-}t\text{-}Bu_2\text{-}4\text{-}MeC_6H_2)]_2$,[7] R_2MMR_2 [M = Al,[8] Ga;[9] R = $-CH(SiMe_3)_2$],

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and $[MeAlN(2,6\text{-}i\text{-}Pr_2C_6H_3)]_3$[10] and a number of species involving bonds to transition metals[15] constitute the extent of currently available structural knowledge. A small number of structures featuring three-coordinate indium have also appeared.[11-13] These studies clearly show that the formation of the electron-deficient, three-coordinate, monomeric compounds requires the use of very bulky ligands to prevent further association involving the sp^2-hybridized Al and Ga centers. In theory, the presence of ligands bearing lone pairs of electrons on atoms directly bound to either Al or Ga should effect reduction of the Lewis acid character of the metal through delocalization into the empty metal p orbital. This process may lead to some multiple character in the metal–ligand bond whose length should decrease as the electron delocalization increases. This theme has been explored by some recent work in this laboratory which has focused on structural characterization of compounds with low coordination numbers and multiple bonding between elements of the third and fifth main groups.[10,16,17] More often than not, however, the presence of electron pairs on ligands bound to Al or Ga leads to association through ligand bridging. Thus, the vast majority of known Al and Ga derivatives of amides, phosphides, arsenides, alkoxides, aryloxides, and thiolates are strongly associated, in this fashion, through bridging to the metal. In only a very few instances are monomeric, low-coordinate complexes obtained.[1,4-7] For thiolate derivatives there appears to be no well-characterized, neutral, monomeric complexes known for either Al or Ga. In this paper, the synthesis and structural characterization of the first such compounds are described.

Experimental Section

General Procedures. All experiments were performed either by the use of modified Schlenk techniques or in a Vacuum Atmospheres HE 43-2 drybox under a nitrogen atmosphere. Solvents were freshly distilled from a Na/K alloy and degassed twice prior to use. ^1H NMR spectra were recorded in C_6D_6 or C_7D_8 solutions by using a General Electric QE-300 spectrometer. Infrared spectra were recorded as a Nujol mull between CsI plates on a Perkin-Elmer PE-1430 spectrometer.

Starting Materials. $GaCl_3$ (Strem) and *n*-BuLi (1.6 M in hexanes) (Aldrich) were obtained commercially and used as received without further purification. $AlBr_3$ (Alfa) was purified by vacuum sublimation. HSMes* (2,4,6-tri-*tert*-butylthiophenol) was prepared according to literature methods,[18-20] and it gave a satisfactory elemental analysis.

Synthesis of Al(SMes*)$_3$ (1). HSMes* (1.114 g, 4 mmol) was dissolved in toluene (25 mL) and treated slowly with *n*-BuLi (2.5 mL of a 1.6 M hexane solution; 4 mmol) with cooling in an ice bath. A white suspension of LiSMes* was formed immediately. The mixture was stirred for 15 min at 0 °C and allowed to warm to room temperature with continuous stirring for 1 h. The suspension of LiSMes* was added slowly to a solution of $AlBr_3$ (0.53 g, 2 mmol) in toluene (20 mL) at room temperature. A slightly exothermic reaction began immediately, which resulted in a clear solution. After ca. 5 min. a white precipitate of LiBr was formed. The mixture was stirred for 18 h at room temperature. Filtration through Celite gave a clear, pale yellow solution. Reduction of the volume under reduced pressure to 20 mL and storage of the solution at room temperature gave colorless crystals suitable for X-ray structure determination. Further reduction of the volume to ca. 10 mL gave a total yield of 0.69 g (40%). Mp: 181–182 °C. ^1H NMR: δ 7.48 (s, 2 H, *m*-H), 1.63 (s, 18 H *o-t*-Bu), 1.34 (s, 9 H, *p-t*-Bu).

Synthesis of Ga(SMes*)$_3$ (2). LiSMes* was prepared by dissolving HSMes* in pentane and slowly adding an equivalent amount of *n*-BuLi at −10 °C. A white suspension was formed immediately; the mixture was stirred for 30 min at −10 °C and allowed to warm to room temperature with continuous stirring for 2 h. The white precipitate was allowed to settle, and the supernatant liquid was removed by a double-tipped needle and discarded. The residue was dried under vacuum to afford a white powder. A 1.28-g (4.5-mmol) sample of the freshly prepared LiSMes* was suspended in toluene (40 mL) and slowly added to a solution of $GaCl_3$ (0.264 g, 1.5 mmol) in toluene (20 mL) at 0 °C. The exothermic reaction started immediately and gave a turbid, pale yellow solution. The mixture was stirred at room temperature for 12 h and then refluxed for another 12 h. Filtration through Celite gave a pale yellow, clear solution. After reduction of the volume to ca. 20 mL, colorless crystals, suitable for X-ray structure determination, were formed at room temperature. Further reduction of the volume to 10 mL gave a total yield of 0.73 g (54%). Mp: 151–153 °C. ^1H NMR: δ 7.50 (s, 2 H, *m*-H), 1.61 (s, 18 H, *o-t*-Bu), 1.34 (s, 9 H, *p-t*-Bu).

Table I. Crystallographic Data[a] for Al(SMes*)$_3$ (**1**) and Ga(SMes*)$_3$ (**2**)

	Al(SMes*)$_3$ (**1**)	Ga(SMes*)$_3$ (**2**)
formula	$C_{54}H_{87}AlS_3$	$C_{54}H_{87}GaS_3$
fw	859.4	902.1
cryst syst	monoclinic	monoclinic
color and habit	colorless parallelepipeds	colorless cubes
space group	$P2_1/n$	$P2_1/n$
a, Å	10.229 (5)	10.243 (2)
b, Å	26.137 (7)	26.189 (2)
c, Å	19.908 (5)	20.031 (3)
β, deg	91.260 (3)	91.554 (1)
V, Å^3	5322 (3)	5371 (2)
Z	4	4
d(calc), g cm^{-3}	1.073	1.116
linear abs coeff, cm^{-1}	1.80	6.52
2θ range, deg	0–55	0–55
no. of obsd reflcns	5644 [$I > 3\sigma(I)$]	8388 [$I > 3\sigma(I)$]
no. of variables	524	522
$R(F)$; $R_w(F)$	0.049; 0.058	0.049; 0.055

[a] Data were collected at 130 K with graphite-monochromated MoKα radiation (λ = 0.71069 Å).

Table II. Atomic Coordinates (×10^5 (**1**); ×10^4 (**2**)) and Isotropic Thermal Parameters (Å^2 × 10^3) for Selected Atoms in the Structures of **1** and **2**

	x	*y*	*z*	*U*[a]
		Compound **1**		
Al(1)	63542 (11)	20998 (4)	15164 (5)	17 (1)
S(1)	56510 (10)	25559 (3)	6676 (4)	23 (1)
S(2)	62172 (9)	12714 (3)	13775 (4)	19 (1)
S(3)	68749 (9)	24929 (3)	24568 (4)	21 (1)
C(1)	56944 (36)	20682 (12)	237 (17)	17 (1)
C(2)	68565 (34)	19992 (13)	−3369 (16)	16 (1)
C(6)	45866 (35)	17547 (13)	−921 (17)	18 (1)
C(101)	70195 (34)	10228 (12)	21260 (17)	17 (1)
C(102)	64056 (34)	10639 (13)	27581 (18)	18 (1)
C(106)	82744 (35)	8021 (12)	20756 (18)	18 (1)
C(201)	78047 (36)	30213 (13)	21229 (16)	17 (1)
C(202)	91776 (36)	29672 (12)	30656 (17)	17 (1)
C(206)	71586 (37)	34733 (13)	19079 (18)	21 (1)
		Compound **2**		
Ga(1)	6372 (1)	2096 (1)	1514 (1)	19 (1)
S(1)	5739 (1)	2559 (1)	649 (1)	25 (1)
S(2)	6194 (1)	1262 (1)	1385 (1)	23 (1)
S(3)	6912 (1)	2491 (1)	2457 (1)	24 (1)
C(1)	5752 (3)	2071 (1)	12 (1)	18 (1)
C(2)	6899 (3)	1997 (1)	−353 (1)	18 (1)
C(6)	4633 (3)	1762 (1)	−101 (1)	21 (1)
C(101)	7014 (3)	1018 (1)	2130 (2)	21 (1)
C(102)	6409 (3)	1060 (1)	2756 (2)	21 (1)
C(106)	8274 (3)	801 (1)	2080 (2)	23 (1)
C(201)	7822 (3)	3020 (1)	2125 (1)	21 (1)
C(202)	9188 (3)	2970 (1)	2059 (1)	21 (1)
C(206)	7173 (3)	3472 (1)	1913 (2)	24 (1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

X-ray Data Collection, Solution, and Refinement of Structures. The crystals of **1** or **2** were transferred from the Schlenk tube onto a Petri dish and immediately covered with a layer of hydrocarbon oil.[21] Single

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Table III. Important Bond Distances (Å) and Angles (deg) and Other Structural Parameters for **1** and **2**

	$Al(SMes^*)_3$ (**1**)	$Ga(SMes^*)_3$ (**2**)
M-S(1)	2.177 (2)	2.197 (1)
M-S(2)	2.191 (2)	2.207 (1)
M-S(3)	2.187 (2)	2.212 (1)
S(1)-C(1)	1.809 (4)	1.806 (3)
S(2)-C(101)	1.806 (4)	1.808 (3)
S(3)-C(201)	1.811 (4)	1.807 (3)
S(1)-M-S(2)	115.1 (1)	115.6 (1)
S(1)-M-S(3)	118.4 (1)	118.5 (1)
S(2)-M-S(3)	125.9 (1)	125.5 (1)
M-S(1)-C(1)	98.7 (1)	99.1 (1)
M-S(2)-C(101)	103.0 (1)	102.6 (1)
M-S(3)-C(201)	99.4 (1)	99.4 (1)
dist of M from the S(1)S(2)S(3) plane	0.09	0.08
shortest M···H dist	2.566	2.679

crystals were selected, mounted on a glass fiber, and immediately placed in the low-temperature N_2 stream. The X-ray data for compound **1** were collected by using a Syntex $P2_1$ diffractometer equipped with a locally modified Syntex LT-1 device and its structure was solved by direct methods. The X-ray data collection for compound **2** was carried out with a Siemens R3 m/V diffractometer, equipped with a locally modified Enraf-Nonius LT apparatus. The structure of **2** was solved by using a Patterson synthesis. Calculations were performed on a Micro Vax 3200 using a SHELXTL-PLUS program system (Version 5). The atomic form factors, including anomalous scattering factors, were taken from the usual sources.[22] An absorption correction was applied using the method described in ref 23. Table I summarizes the crystal data and refinement for both data collections. Important atom coordinates, bond distances, and angles are presented in Tables II and III. Hydrogen atoms within a 3-Å radius of the metal centers were located on a difference map and refined. One *t*-Bu group (the *p*-*t*-Bu group of the C(103) aromatic ring) in **1** and **2** was disordered over two different sites. It was refined satisfactorily at a 50% occupancy of each site.

Results and Discussion

Syntheses. Owing to the tendency of $AlBr_3$ and $GaCl_3$ to form adducts, the syntheses were performed with the exclusion of donor solvents such as ethers. $Al(SMes^*)_3$ (**1**) was prepared by the reaction of $AlBr_3$ with LiSMes* in the ratio of 1:2 in toluene. To date it has not proved possible to obtain the compound by using 3 equiv of the lithium thiolate per aluminum. This suggests that a disproportion mechanism such as

$$2AlBr_3 + 4LiSMes^* \xrightarrow{\text{toluene}} Al(SMes^*)_3 + Br_2Al(SMes^*) + 4LiBr \quad (1)$$

probably occurs. It is not yet clear why the treatment of $AlBr_3$ with 3 equiv of LiSMes* does not afford the obvious trisubstituted product. Attempts to isolate the dibromo(thiolato)aluminum compound at low temperatures were also unsuccessful. Presumably the desired compound was formed, but because of its instability it could not be isolated, even at low temperature.

$Ga(SMes^*)_3$ (**2**) was prepared by a straightforward synthesis involving the reaction of $GaCl_3$ and LiSMes* in the ratio 1:3 in toluene:

$$GaCl_3 + 3LiSMes^* \xrightarrow{\text{toluene}} Ga(SMes^*)_3 + 3LiCl \quad (2)$$

It was necessary to isolate the lithium salt of HSMes* to avoid the presence of any excess of *n*-BuLi in the reaction depicted by eq 2. All attempts with in situ formation of the lithium thiolate yielded only $(Mes^*S)_2Ga(n\text{-}Bu)$.[14]

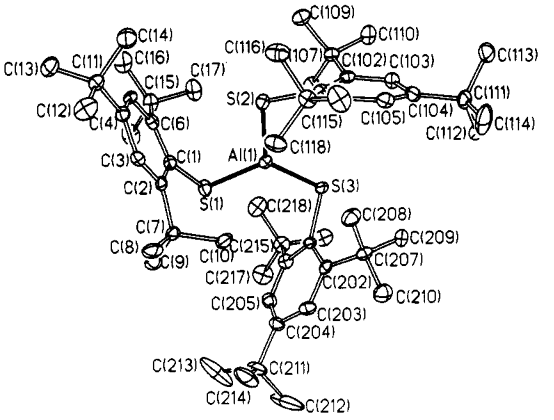

Figure 1. Computer-generated plot of **1** (50% ellipsoids). H atoms are omitted for clarity.

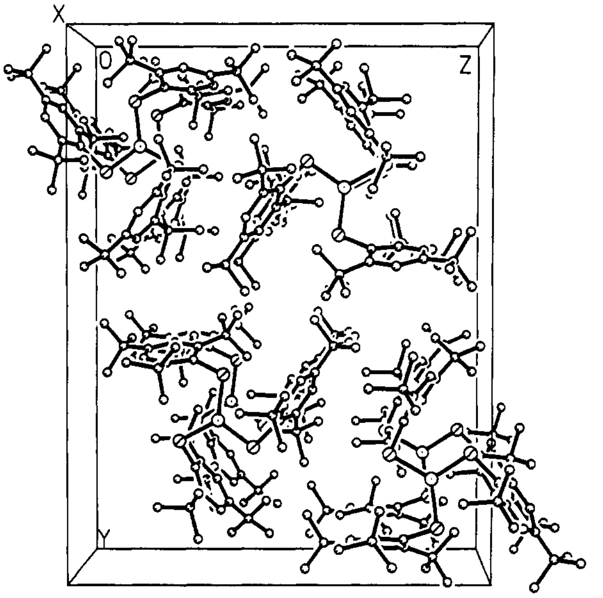

Figure 2. Computer-generated plot of the unit cell of **2**. Axis is doubled to show the packing. H atoms are omitted for clarity.

Structural Descriptions. $Al(SMes^*)_3$ (1). The molecular structure of **1** is illustrated in Figure 1. It comprises discrete molecules of $Al(SMes^*)_3$ units that are well-separated from each other and have no crystallographic symmetry. The three-coordinate aluminum atom is located slightly above (0.09 Å) the plane of the three sulfur atoms. The angles deviate from a regular trigonal coordination by up to 5°, although the sum of the angles at Al is 359.4°. The average Al-S distance is 2.185 (8) Å, and the average S-C distance is 1.809 (6) Å. The aromatic rings of the $[SMes^*]^-$ ligands form an irregular propeller-like arrangement around the S_3 plane with angles of 87.4, 70.5, and 89.6° between each aromatic ring and the sulfur plane. The ipso carbons are located 0.4384, 0.2682, and 1.1574 Å from the plane defined by the three sulfurs, such that angles of 14.0, 8.5, and 39.7° are formed between this plane and the S-C vectors. The Al-S-C angles average 100.4°. For all three aromatic rings there is an angle between the average ring plane and the S-C(ipso) vector. For the rings attached to S(1) and S(2) the angles are 8.6 and 13.6°. Moreover, the bending of the rings is toward the Al. For the remaining ring bound to S(3), the angle is 13.1° and the bending is away from the metal. The shortest Al···H approaches involve H(3) at 2.72 Å, H(1) at 2.841 Å, and H(2) at 2.969 Å. There are no significant geometrical distortions apparent in the corresponding *t*-Bu groups.

$Ga(SMes^*)_3$ (2). This species is isomorphous to the corresponding Al compound. Its structure, whose unit cell is illustrated in Figure 2, has an almost planar trigonal GaS_3 core. The Ga atom is situated 0.08 Å above the S(1)S(2)S(3) plane. The sum

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[22] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974, Vol IV.

[23] The absorption correction was made using the program XABS by H. Hope and B. Moezzi. The program obtains an absorption tensor from $F_o - F_c$ differences. Moezzi, B. Ph.D. Dissertation, University of California, Davis, 1987.

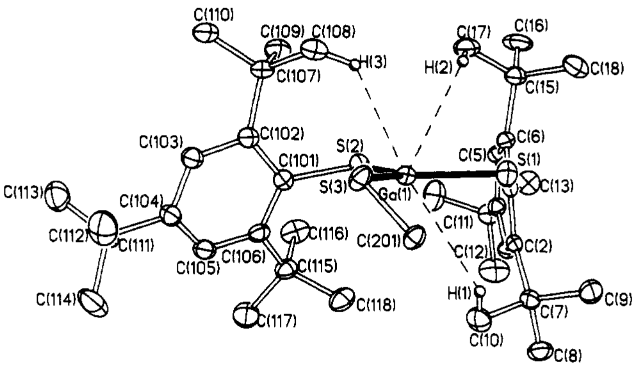

Figure 3. Drawing of **2** illustrating the closest Ga···H interactions involving the *o*-*t*-Bu groups. For clarity the Mes* group attached to S(3) is not displayed.

Table IV. Important IR Stretching Frequencies (cm^{-1}) for the M–S(thiolate) Bonds in Three- and Four-Coordinate Aluminum and Gallium Thiolate Compounds

compound	metal coord. no.	ν, cm^{-1}	ref
Al(SMes*)$_3$	3	547	*a*
(Mes*S)$_2$Al(*n*-Bu)	3	544	14
Al[S(2,4,6-*i*-Pr$_3$C$_6$H$_2$)]$_3$·THF	4	475	14
Ga(SMes*)$_3$	3	398	*a*
(Mes*S)$_2$Ga(*n*-Bu)	3	398	14
Ga{S(2,4,6-*i*-Pr$_3$C$_6$H$_2$)}$_4$·Li(OEt$_2$)	4	310–340	14
[GaPh$_2$SEt]$_2$	4	325–315	35

[a] This work.

of S–Ga–S angles is 359.6°, although angles at Ga deviate up to 5° from an ideal trigonal coordination. The Ga–S bond distances range from 2.197 (1) to 2.212 (1) Å. The angles between the S(1)S(2)S(3) plane and the three aromatic rings are 85.5, 72.3, and 88.3°, respectively. The ipso carbons are located 0.4257, 0.3328, and 1.0944 Å from the plane of the sulfurs, and the angles between the S–C vectors and this plane are 13.6, 10.6, and 37.3°. As in the case of **1** there are angles of 8.9, 12.9, and 13.1° between the S(1)–C(1), S(2)–C(101), and S(3)–C(201) vectors and their respective aromatic ring planes. In addition, the bending is away from rather than toward the metal except in the case of the C(201) ring. The shortest Ga···H distances are 2.691 Å, involving H(1), 2.91 Å to H(2), and 2.973 Å to H(3). These possible interactions are illustrated in Figure 3. There are no observable distortions in the geometries of the relevant *t*-Bu groups.

Infrared Spectroscopy. On the basis of the comparison of the vibrational spectrum of HSMes* with the title compounds, the Al–S and Ga–S stretching frequencies may be assigned to the moderately strong bands that appear at 547 cm^{-1} for Al(SMes*)$_3$ and at 398 cm^{-1} in the case of Ga(SMes*)$_3$. In approximate C_{3h} symmetry, the M–S$_3$ stretching modes of the AlS$_3$ and GaS$_3$ core are A′ (Raman active) and E′ (IR and Raman active). The vibrational spectra are in accordance with this symmetry. IR data for 1 and 2 and related Al and Ga thiolates are provided in Table IV.

Discussion

Although coordination number 3 in metal complexes is becoming more common throughout the periodic table, it remains relatively uncommon in the heavier main-group 3 elements. This is a reflection of the relatively high Lewis acidity of these metal centers (especially Al), which is conducive to the formation of complexes with either higher coordination numbers or the association of the monomers themselves. In the solid-state, three-coordination for metals is generally observed only when very bulky substituents such as –N(SiMe$_3$)$_2$, –CH(SiMe$_3$)$_2$, –O(2,6-*t*-Bu$_2$-4-MeC$_6$H$_2$), mesityl (Mes), –EMes$_2$ (E = P or As), or –P(H)Mes* are present. With the exception of the latter groups, the atom attached to the metal is O, N, or C bearing, respectively, one, two, or three organic substituents. The small size of these atoms ensures a generally more crowded environment close to the metal, which blocks an increase in the coordination number. Ligands that involve an atom from the second row attached to the metal generally require much larger substituents to effect the same degree of crowding. For this reason there exist very few, low-coordinate (three or less) neutral, metal derivatives of phosphide (–PR$_2$) or thiolate (–SR) ligands throughout the periodic table. Recent exceptions for thiolate derivatives include species such as [Sn(SMes*)$_2$]$_2$,[24] [Cd(SMes*)$_2$]$_2$,[25] [M(SMes*)$_2$]$_2$ (M = Mn, Fe, Co),[26] and Et$_2$OZn(SMes*)$_2$.[27] The monomeric structure of the lithium salt (THF)$_3$LiSMes*[28] also underscores the large size of the –SMes* ligand. The work described in this paper further supports the high steric requirements of the –SMes* group. Most notably, complexes **1** and **2** are the first three-coordinate thiolate complexes of Al or Ga to be characterized by X-ray crystallography.

Table V. Variation of the M–S(thiolate) Bond Distance (Å) with Coordination Number in Aluminum and Gallium Chalcogenides

compound	coord no. M	coord no. E[a]	bond length, Å	ref
Al(SMes*)$_3$	3	2	2.185 (7)	*b*
(Mes*S)$_2$Al(*n*-Bu)	3	2	2.19 (1)	14
(Me$_2$AlSMe)$_n$	4		2.348	29
[Me$_2$AlSC$_6$F$_5$]$_2$	4	4	2.405 (8)	31
AlMe[O(2,6-*t*-Bu$_2$-4-MeC$_6$H$_2$)]$_2$	3	2	1.686 (2)	7
[Al{O(*t*-Bu)}(*t*-Bu)$_2$]$_2$	4	3	1.882 (4)	14
Ga(SMes*)$_3$	3	2	2.205 (6)	b
(Mes*S)$_2$Ga(*n*-Bu)	3	2	2.21 (1)	14
[GaPh$_2$SEt]$_2$	4	3	2.379 (3)	35
[(*n*-Pr)$_4$N][Ga(SEt)$_4$]	4	2	2.264 (3)	36

[a] E = O or S. [b] This work.

Complexes **1** and **2** are of further interest because thiolate derivatives of these elements have, in general, received little attention. Only a few such complexes have been structurally characterized.[42] These include the polymeric species [Me$_2$Al(SMe)]$_n$,[29] the dimeric compounds Me$_2$Al(μ-PyS)$_2$AlMe$_2$[30] and [Me$_2$AlSC$_6$F$_5$]$_2$,[31] the tetrameric Al$_4$I$_4$(SMe)$_4$,[32] the gallium species Ga$_4$I$_4$(SMe)$_4$S$_2$,[33] [GaI$_2$(SMe)]$_2$,[34] and [GaPh$_2$SEt]$_2$,[35] and the ionic compounds [N(*n*-Pr)$_4$][Ga(SEt)$_4$], [NEt$_4$][Ga(SPh)$_4$],[36] and [NEt$_4$]$_2$[Ga$_2$S$_2$(SPh)$_4$].[36] The average Al–S bond length in **1** is 2.185 (8) Å which is shorter, by a large margin, than those observed in other aluminum thiolate complexes such as [Me$_2$AlSMe]$_n$ (2.348 (2), 2.37 Å in the gas phase[29]) or [Me$_2$AlSC$_6$F$_5$]$_2$ (2.405 (8) Å).[31] Part of this shortening is, no doubt, due to the lower coordination number of the metal and the sulfur in **1**. In addition, there is the possibility of a π-interaction between the empty metal p orbital and the lone pairs of the sulfur atom. No evidence for such an interaction was observed in either **1** or **2**. Thus, a variable-temperature ^{1}H NMR study of **1** and

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2 between room temperature and −90 °C revealed no dynamic behavior that could be indicative of restricted rotation around an M–S bond.

The average Ga–S bond length 2.205 (1) Å is only marginally (0.02 Å) longer than the corresponding Al–S distance. This observation is in accordance with the very similar size of Al and Ga.[37] In contrast to the Al–S distances in **1**, and Ga–S bond lengths in **2** are not a great deal shorter than those seen in the four-coordinate anions $[Ga(SPh)_4]^-$ (2.257 (8) Å) and $[Ga(SEt)_4]^-$ (2.264 (3) Å).[36] Somewhat longer Ga–S distances ranging from about 2.36 to 2.40 Å were observed in the case of the bridging thiolate complexes $Ga_4I_4(SMe)_4S_2$,[33] $Ga_2I_4(SMe)_2$,[34] and $[GaPh_2SEt]_2$.[35] In all complexes and in the Al derivatives, there is a clearly defined dependence of the M–S distance on the coordination of the metal and the sulfur as is illustrated in Table V.

Further interesting features of the structures of **1** and **2** are the slight deviation of the geometry at the metal centers from planarity, the angles between the S–C vectors and the S(1)S(2)S(3) plane, and the bending of the SC(ipso) vectors from the plane of the aromatic rings. It can be seen from Figure 3 that the three aromatic rings are all located on one side of the plane defined by the three sulfurs. Moreover, the metal apex of the very flattened trigonal pyramid defined by the metal and the three sulfurs is projected to the same side of the plane as the three aromatic rings. It is also notable that the two aromatic rings that are bent toward the metal are those involving C(1) and C(101) (Figures 1 and 2). Oddly, these rings are the most sterically crowding for the metal center because the angles between the S(1)C(1) and S(2)C(101) and the plane of the sulfurs are far lower (by 25°) than the angle for the S(3)C(201) vector. Significantly, perhaps, the S(1)–M–S(2) angle is the lowest of the three SMS angles at the metals.

These minor distortions in the structures may be most easily interpreted on the basis of a significant ionic contribution to the M–S bonding for **1** and **2**. The bending of the C(1) and C(101) aromatic rings toward the metal may be caused by the M···H interactions involving the *o*-*t*-Bu groups of these ligands (Figure 3). In the case of **1**, the closest (<3 Å) Al···H approaches involve hydrogens H(1), H(2), and H(3) from the C(1) and C(101) rings. For **2**, the Ga···H interaction involves H(1), H(2), and H(3) from the C(1) and C(101) rings. Thus, all the M···H interactions in **1** and **2** involve groups in the C(1) and C(101) rings—the ones that are bent toward the metals. Moreover, the M···H distances involved are near the sum of the van der Waals radii (2.5–2.8 Å)[38] for M and H. An alternative explanation of the bending of the aromatic rings toward the metal center could involve crystal packing, which tends to align the aromatic groups in neighboring molecules in a parallel fashion.[27]

The short M–S distances are clearly indicative of strong M–S interactions in both compounds. The infrared spectra of **1** and **2** also provide evidence for strong M–S bonds. It is apparent from Table IV that the M–S stretching frequencies for **1** and **2** are significantly higher than those observed for the four-coordinate species (Table IV). A comparison of the data with data for other unpublished three-coordinated aluminum and gallium thiolate compounds[14] reveals very similar values for the M–S stretching frequencies. The high M–S frequencies observed for **1** and **2** could be interpreted on the basis of a π-interaction between the metal and sulfur ligand. However, the lack of any correlation between the M–S distance and the angle between the S–C bonds and the S(1)S(2)S(3) plane does not support this view. Also, the very similar values of the M–S stretching frequencies in the related three-coordinate complexes in Table IV lend little support to a M–S π-bonding scenario because the π-bond strength should depend heavily on the number of sulfurs with which the empty metal p orbital interacts. As already mentioned, variable-temperature ^1H NMR data show no dynamic behavior that would support the presence of restricted rotation about the M–S bond. In effect the spectroscopic and structural data favor more ionic M–S bonding. The structural manifestations (slightly pyramidal coordination) of ionic bonding seen in both **1** and **2** and further metal–ligand interactions have been observed previously in a number of three-coordinate lanthanide amides and alkyls.[39–41] These interesting complexes are often characterized by much larger deviations from planarity and stronger M···H interactions. However, the structures of **1** and **2** are apparently the first examples in which such ionic structural distortions have been recognized for three-coordinate metal derivatives of second-row ligands.

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Supplementary Material Available: Full tables of data collection parameters and further details of refinement, atomic coordinates and equivalent isotropic thermal parameters, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters (20 pages); tables of structure factors (66 pages). Ordering information is given on any current masthead page.

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