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Article

Synthesis and Characterization of Aluminum-Containing Tin(IV) Heterobimetallic Sulfides

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Three novel aluminum-containing tin(IV) heterobimetallic sulfides are reported. The reaction of $[LAl(SLi)_2(THF)_2]_2$ (**1**) [L = $HC(CMeNAr)_2$, Ar = 2,6-$i$$Pr_2C_6H_3$] with Ph_2SnCl_2, Me_2SnCl_2, and $SnCl_4$ in THF respectively afforded $LAl(\mu\text{-}S)_2SnPh_2$ (**2**), $LAl(\mu\text{-}S)_2SnMe_2$ (**3**), and $LAl(\mu\text{-}S)_2Sn(\mu\text{-}S)_2AlL$ (**4**) in moderate yields. Compounds **2**, **3**, and **4** were characterized by elemental analysis, NMR, electron-impact mass spectrometry, and single-crystal X-ray structural analysis.

Introduction

Organometallic chalcogen compounds have attracted much interest because of their application as catalysts in industry. More recently, attention has been paid to heterobimetallic chalcogen compounds not only from the viewpoint of fundamental chemistry but also because of their catalytic properties.[1] Aluminum is the most abundant metal in the earth's crust; therefore, many aluminum-containing heterobimetallic oxides have been synthesized and characterized.[2] Organometallic sulfides are less stable than the corresponding oxides, and synthetic methods for their preparation are limited. Moreover, aluminum-containing heterobimetallic sulfides have not been reported very often. There are only a few examples known containing the $Al-(\mu\text{-}S)-Fe$[3] and $Al-(\mu\text{-}S)-M$ (M = Zr and Ti) moieties.[4,5] Recently, $[LAl(SLi)_2(THF)_2]_2$ (**1**) was prepared, and this is a valuable precursor for the preparation of heterobimetallic sulfides.[4] The first aluminum-containing heterotrimetallic sulfide of composition $L_2Al_2Ge_4Li_2S_7$ has been prepared by reacting **1** with $GeCl_2$·dioxane.[6] Herein, we report on the reaction of **1** with organotin dichlorides and tin tetrachloride to yield $LAl(\mu\text{-}S)_2SnR_2$ (R = Me and Ph) and the spirocyclic heterotrimetallic sulfide $LAl(\mu\text{-}S)_2Sn(\mu\text{-}S)_2AlL$.

Experimental Section

General Procedures. All manipulations were carried out under a purified nitrogen atmosphere using Schlenk techniques or inside a Mbraun MB 150-GI glovebox. All solvents were distilled from Na/benzophenone ketyl prior to use. Commercially available chemicals were purchased from Aldrich or Fluka and used as received. $SnCl_4$·2THF (THF = tetrahydrofuran) was prepared according to a literature procedure.[7] Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. ^1H, ^{13}C, ^{27}Al, and ^{119}Sn NMR

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10.1021/ic052139m CCC: $33.50

Table 1. Crystallographic Data for Compound **2**, **3**, **3a**, and **4**

	2·toluene	**3**	**3**·toluene (**3a**)	**4**·$1.5C_7H_8$·1THF
formula	$C_{48}H_{59}AlN_2S_2Sn$	$C_{31}H_{47}AlN_2S_2Sn$	$C_{38}H_{55}AlN_2S_2Sn$	$C_{72.5}H_{102}Al_2N_4OS_4Sn$
fw	873.76	657.50	749.64	1346.47
temp (K)	133(2)	294(2)	133(2)	133(2)
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	9.543(1)	10.502(2)	8.808(2)	12.342(1)
b (Å)	23.398(1)	26.736(4)	13.280(3)	18.604(1)
c (Å)	20.409(1)	12.615(3)	17.283(4)	30.762(1)
α (deg)	90	90	79.57(3)	90
β (deg)	95.74(1)	104.74(3)	75.42(3)	92.44(1)
γ (deg)	90	90	87.69(3)	90
V (Å^3)	4534(1)	3426(1)	2061(1)	7057(1)
Z	4	4	2	4
ρ_c (Mg/m^3)	1.280	1.275	1.294	1.267
M (mm^{-1})	0.709	0.914	0.823	0.550
F(000)	1824	1368	784	2852
Θ range (deg)	1.74−24.84	1.83−25.03	1.56−24.84	1.65−24.83
index ranges	$-11 \le h \le 9$	$-12 \le h \le 12$	$-10 \le h \le 10$	$-14 \le h \le 14$
	$-27 \le k \le 27$	$-31 \le k \le 31$	$-15 \le k \le 15$	$-21 \le k \le 21$
	$-24 \le l \le 24$	$-15 \le l \le 15$	$-20 \le l \le 20$	$-36 \le l \le 36$
no. of reflns collected	64304	27934	34091	103650
no. of independent $R_{(int)}$	7812 (0.0546)	6042 (0.0438)	6640 (0.0576)	12130 (0.0838)
no. of data/restraints/params	7812/0/486	6042/0/349	6640/0/410	12130/1279/767
GOF/F^2	0.988	1.037	1.017	1.014
$R1^a$, $wR2^b$[$I > 2\sigma(I)$]	0.0312, 0.0760	0.0446, 0.1034	0.0274, 0.0677	0.0780, 0.2297
$R1^a$, $wR2^b$(all data)	0.0443, 0.0795	0.0586, 0.1106	0.0352, 0.0700	0.1115, 0.2509

spectra were recorded on Bruker AM 300 and 500 spectrometers and IR spectra on a Bio-Rad Digilab FTS-7 spectrometer. Electron-impact mass spectra (EI-MS) were measured on a Finnigan MAT 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes and were not corrected.

Preparation of LAl(μ-S)$_2$SnPh$_2$ (2). A solution of Ph_2SnCl_2 (0.69 g, 2 mmol) in THF (10 mL) was added dropwise to a solution of **1** (1.33 g, 1 mmol) in THF (20 mL) at −30 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature. The solvent was removed in vacuo. The solid was extracted with toluene (10 mL), and the extract was kept at room temperature for 2 days to afford **2** as colorless crystals. Yield: 1.42 g (91%). mp: 251 °C. EI-MS m/z (%): 782 (40) [M^+], 705 (100) [$M^+ -$ Ph], 627 (30) [$M^+ -$ 2Ph]. ^{1}H NMR (300.13 MHz, C_6D_6, 25 °C, TMS): δ (ppm) 7.23−7.16 (m, 6 H, Ar-*H*), 7.10−7.02 (m, 10 H, *Ph*-Sn), 4.90 (s, 1 H, γ-*H*), 3.55 (sept, $^3J_{H-H} = 6.8$ Hz, 4 H, C*H*Me$_2$), 1.60 (s, 6 H, *Me*), 1.49 (d, $^3J_{H-H} = 6.8$ Hz, 12 H, CH*Me*$_2$), 1.12 (d, $^3J_{H-H} = 6.8$ Hz, 12 H, CH*Me*$_2$). ^{13}C NMR (75.48 MHz, C_6D_6, 25 °C, TMS): δ (ppm) 170.9 (*C*N), 145.1, 141.3, 139.5, 136.0, 129.3, 125.6, 124.9 (*Ar* and Sn-*Ph*), 98.1 (γ-*C*), 29.2 (*C*HMe$_2$), 25.4 (CH*Me*$_2$), 23.9 (CH*Me*$_2$), 21.4 (*Me*). ^{27}Al NMR (78.21 MHz, C_6D_6, 25 °C, $AlCl_3$·$6H_2O$): δ (ppm) 114.5. ^{119}Sn NMR (186.49 MHz, C_6H_6, 25 °C, $SnMe_4$): δ (ppm) −38. Anal. Calcd for $C_{41}H_{51}AlN_2S_2Sn$·$^1/_4C_7H_8$ (804.66): C, 63.88; H, 6.59; N, 3.48. Found: C, 63.92; H, 6.70; N, 3.35%.

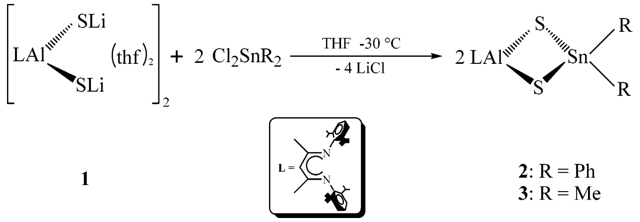
Preparation of LAl(μ-S)$_2$SnMe$_2$ (3). The preparation of **3** is like that of **2** except from Me_2SnCl_2 (0.44 g, 2 mmol) and **1** (1.33 g, 1 mmol). Product **3** was isolated as colorless crystals. Yield: 1.184 g (90%). mp: 214−215 °C. EI-MS m/z (%): 658 (20) [M^+], 643 (100) [$M^+ -$ Me], 627 (5) [$M^+ -$ 2Me]. ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 7.25−7.17 (m, 6 H, Ar-*H*), 5.25 (s, 1 H, γ-*H*), 3.32 (sept, $^3J_{H-H} = 6.8$ Hz, 4 H, C*H*Me$_2$), 1.84 (s, 6 H, *Me*), 1.36 (d, $^3J_{H-H} = 6.8$ Hz, 12 H, CH*Me*$_2$), 1.12 (d, $^3J_{H-H} = 6.8$ Hz, 12 H, CH*Me*$_2$), 0.40 (s, 6 H, $^2J_{(117)Sn-H} = 1.4$ Hz, $_2J_{(119)Sn-H} = 1.4$ Hz, *Me*-Sn). ^{13}C NMR (75.48 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 170.7 (*C*N), 144.7, 138.9, 127.0, 124.1 (*p*-, *m*-, *o*-, *i*-*C* of Ar), 98.0 (γ-*C*), 28.9 (*C*HMe$_2$), 26.0 (CH*Me*$_2$), 23.6 (CH*Me*$_2$), 21.5 (*Me*), 2.6 (Sn-*Me*). ^{27}Al NMR (78.21 MHz, $CDCl_3$, 25 °C, $AlCl_3$·$6H_2O$): δ (ppm) 114. ^{119}Sn NMR (186.49 MHz, $CDCl_3$, 25 °C, $SnMe_4$): δ (ppm) 133. Anal. Calcd for $C_{31}H_{47}AlN_2S_2Sn$ (657.52): C, 56.63; H, 7.20; N, 4.26. Found: C, 56.24; H, 7.56; N 3.96%.

Preparation of LAl(μ-S)$_2$Sn(μ-S)$_2$AlL (4). $SnCl_4$ (0.26 g, 0.12 mL, 1 mmol) was added dropwise to a solution of **1** (1.33 g, 1 mmol) in THF (20 mL) at −30 °C. After the addition was complete, the reaction mixture was allowed to warm to room temperature. The solvent was removed in vacuo. The solid was extracted with toluene (10 mL) and kept at room temperature for 2 days to afford colorless crystals. Yield: 0.97 g (85%).

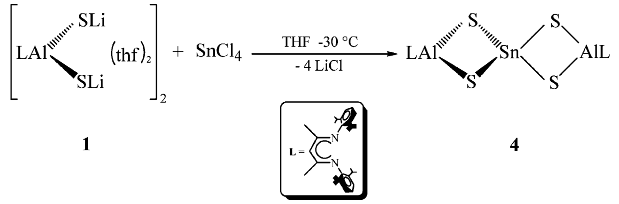
Alternative Preparation of LAl(μ-S)$_2$Sn(μ-S)$_2$AlL (4). 1 (1.33 g, 1 mmol) and $SnCl_4$·2THF (0.41 g, 1 mmol) were mixed as solids in a flask. The flask was placed in liquid nitrogen, and toluene (50 mL) was added slowly. The reaction mixture was allowed to warm to ambient temperature and was stirred overnight. The resulting suspension was filtered, and all volatiles from the filtrate were removed in vacuum to leave a residue that was washed with hexane to give 1.1 g of microcrystalline **4**. Yield: 97%. mp: 321 °C. EI-MS m/z (%): 1136.4 (12) [M^+], 403 (100) [L-Me]. ^{1}H NMR (300.13 MHz, C_6D_6, 25 °C, TMS): δ (ppm) 7.17−7.05 (m, 12 H, Ar-*H*), 4.73 (s, 2 H, γ-*H*), 3.35 (sept, $^3J_{H-H} = 6.8$ Hz, 8 H, C*H*Me$_2$), 1.46 (s, 12 H, *Me*), 1.44 (d, $^3J_{H-H} = 6.8$ Hz, 24 H, CH*Me*$_2$), 1.05 (d, $^3J_{H-H} = 6.8$ Hz, 24 H, CH*Me*$_2$). ^{13}C NMR (75.48 MHz, C_6D_6, 25 °C, TMS): δ (ppm) 171.0 (*C*N), 144.5, 138.9, 129.3, 124.7 (*p*-, *m*-, *o*-, *i*-*C* of Ar), 98.4 (γ-*C*), 29.0 (*C*HMe$_2$), 25.9 (CH*Me*$_2$), 23.8 (CH*Me*$_2$), 21.4 (*Me*). ^{27}Al NMR (78.21 MHz, C_6D_6, 25 °C, $AlCl_3$·$6H_2O$): δ (ppm) 114. ^{119}Sn NMR (186.49 MHz, C_6H_6, 25 °C, $SnMe_4$): δ (ppm) 5.0. Anal. Calcd for $C_{58}H_{82}Al_2N_4S_4Sn$ (1136.40): C, 61.31; H, 7.27; N, 4.93. Found: C, 60.96; H, 6.98; N, 4.50.

Single-Crystal X-ray Structure Determination and Refinement. The crystallographic data for compounds **2**·toluene, **3**·toluene, and **4**·1.5toluene·THF were collected on a Stoe IPDS II array detector system, whereas the data collection for compound **3** was performed on a Bruker three-circle diffractometer equipped with an Apex CCD area detector. Graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) was used in all four experiments.

Scheme 1. Preparation of Compounds **2** and **3**



Scheme 2. Preparation of Compound **4**



The structures were solved by direct methods (SHELXS-90)[8] and refined against F^2 using SHELXL-97.[9] In the case of **4**, the molecule is well-defined, but global anisotropic displacement parameter restraints were used to identify spurious solvents near crystallographic axes. Toluene was treated as a rigid body, and THF was refined using SAME/SADI restraints. Hydrogen atoms were included in geometrically idealized positions and refined isotropically using the riding model with U_{iso} tied to the U_{iso} of the parent atoms. A summary of cell parameters, data collection, structure solution, and refinement for all structures is given in Table 1.

Results and Discussion

Compounds **2** and **3** were prepared by adding dropwise, in THF, Ph_2SnCl_2 or Me_2SnCl_2, respectively, to **1** in THF at low temperature (Schemes 1 and 2). Because $SnCl_4$ is a liquid, it was added directly to the THF solution of **1**. Compound **1** is sparingly soluble in THF, and therefore, it formed a suspension in THF at low temperature. However, after adding Ph_2SnCl_2, Me_2SnCl_2, or $SnCl_4$, the suspension became clear and the light yellow color turned very quickly to colorless. This is an indication for the progress of the reaction. Alternatively, compound **4** can be prepared by the direct reaction of **1** and $SnCl_4 \cdot 2THF$ in toluene to avoid the decomposition of **1** by traces of free HCl present in $SnCl_4$. Compounds **2**, **3**, and **4** are all colorless solids and are well-soluble in toluene, benzene, and so forth. They were characterized by EI-MS spectra; elemental analysis; ^{1}H, ^{13}C, ^{27}Al, and ^{119}Sn NMR investigations; and single-crystal X-ray diffraction studies. The ^{1}H NMR spectra of **2**, **3**, and **4** exhibit one set of resonances for the ligand (L). Compound **2** shows the Sn-Ph resonances in the range from δ 7.10 to 7.02 ppm, which are distinct from those of the Ar-H resonances (δ 7.23−7.16 ppm). Compound **3** exhibits a Sn-Me at δ 0.40 ppm in a 6:1 ratio to that of the γ-H proton. Compound **4** displays only one set of resonances for the ligand (L), indicating that the two ligands are in the same chemical environment. The ^{27}Al NMR spectra of **2**−**4** show the resonances in a narrow range (113−114 ppm), and these are comparable to those of compounds with four-coordinate aluminum.[10] The electron impact mass spectra of **2**, **3**, and **4** (m/z = 782, 658, and 1136) show the parent ion [M^+] with its isotopic pattern. Particularly interesting is the ion of composition [$LAl(\mu\text{-}S)_2Sn$] (m/z = 627), which appears in the fragmentation of both **2** and **3**.

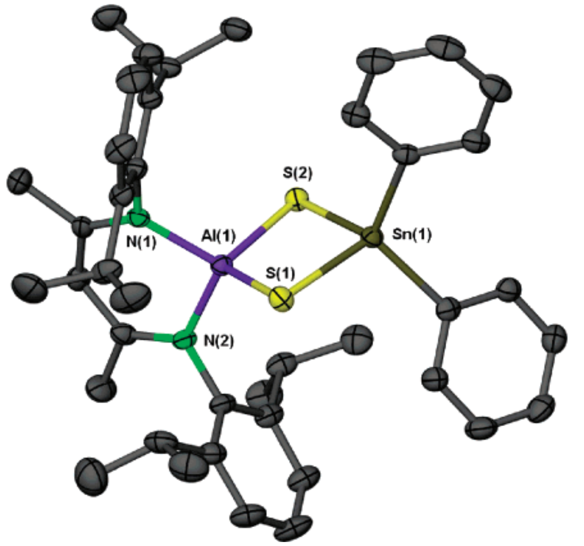


Figure 1. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50% level. The solvent molecule and hydrogen atoms are omitted for clarity.

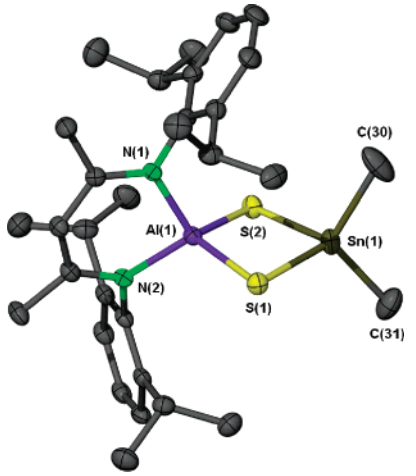


Figure 2. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% level. The solvent molecule and hydrogen atoms are omitted for clarity.

The compositions of **2**, **3**, and **4** were assigned by X-ray structural analysis. Colorless crystals of **2**·toluene, **3**·toluene, and **4**·1.5toluene·THF were obtained from toluene at −28 °C, whereas the solvent-free form of **3** was obtained by its crystallization from hexane at −32 °C. The structure of **4**·1.5toluene·THF contains disordered solvent molecules, which could be refined using restraints and rigid body constraints. Some data collection and refinement details are

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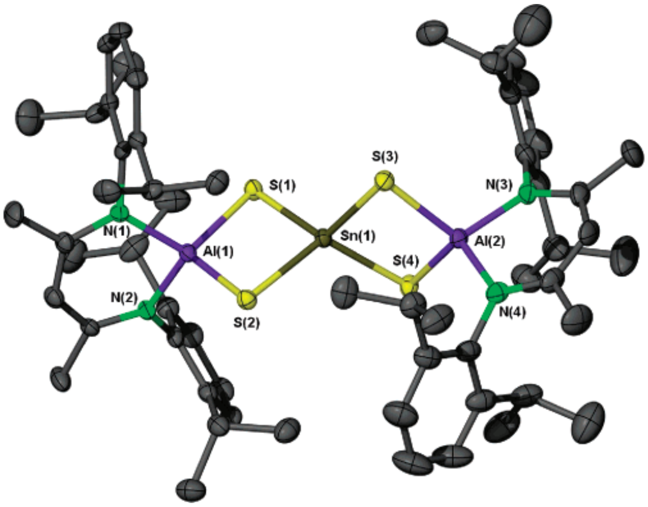

Figure 3. Molecular structure of **4**. Thermal ellipsoids are drawn at the 50% level. The solvent molecule and hydrogen atoms are omitted for clarity.

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

Al(1)−N(1)	1.882(2)	Al(1)−N(2)	1.889(2)
Al(1)−S(1)	2.233(1)	Al(1)−S(2)	2.229(1)
Sn(1)−S(1)	2.403(1)	Sn(1)−S(2)	2.402(1)
Al(1)−Sn(1)	3.026(1)	S(1)−Al(1)−S(2)	103.3(1)
Al(1)−S(1)−Sn(1)	81.4(1)	Al(1)−S(2)−Sn(1)	81.5(1)
S(2)−Sn(1)−S(1)	93.5(1)	C(31)−Sn(1)−C(41)	117.0(1)

Table 3. Selected Bond Distances (Å) and Angles (deg) for Compounds **3** and **3a**

Compound **3**			
Al(1)−N(1)	1.902(3)	Al(1)−N(2)	1.893(3)
Al(1)−S(1)	2.227(1)	Al(1)−S(2)	2.213(1)
Sn(1)−S(1)	2.413(1)	Sn(1)−S(2)	2.395(1)
Al(1)−Sn(1)	3.037(1)	S(2)−Al(1)−S(1)	102.9(1)
Al(1)−S(1)−Sn(1)	81.7(1)	Al(1)−S(2)−Sn(1)	82.4(1)
S(2)−Sn(1)−S(1)	92.5(3)	C(30)−Sn(1)−C(31)	111.8(2)
Compound **3a**			
Al(1)−N(1)	1.906(2)	Al(1)−N(2)	1.882(2)
Al(1)−S(1)	2.234(1)	Al(1)−S(2)	2.225(1)
Sn(1)−S(1)	2.410(1)	Sn(1)−S(2)	2.414(1)
Al(1)−Sn(1)	3.063(1)	S(1)−Al(1)−S(2)	101.9(1)
Al(1)−S(1)−Sn(1)	82.5(1)	Al(1)−S(2)−Sn(1)	82.5(1)
S(1)−Sn(1)−S(2)	91.8(1)	C(30)−Sn(1)−C(31)	112.1(2)

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

Al(1)−N(1)	1.875(6)	Al(1)−N(2)	1.884(6)
Al(2)−N(3)	1.882(6)	Al(2)−N(4)	1.882(6)
Al(1)−S(1)	2.239(3)	Al(1)−S(2)	2.239(3)
Al(2)−S(3)	2.230(3)	Al(2)−S(4)	2.253(3)
Sn(1)−S(1)	2.397(2)	Sn(1)−S(2)	2.378(2)
Sn(1)−S(3)	2.388(2)	Sn(1)−S(4)	2.392(2)
Sn(1)−Al(1)	3.037(2)	Sn(1)−Al(2)	3.035(2)
S(1)−Al(1)−S(2)	102.2(1)	S(3)−Al(2)−S(4)	102.0(1)
Al(1)−S(1)−Sn(1)	81.8(1)	Al(1)−S(2)−Sn(1)	82.2(1)
Al(2)−S(3)−Sn(1)	82.1(1)	Al(2)−S(4)−Sn(1)	81.6(1)
S(1)−Sn(1)−S(2)	93.7(1)	S(3)−Sn(1)−S(4)	93.6(1)
S(1)−Sn(1)−S(4)	122.0(1)	S(2)−Sn(1)−S(3)	119.4(1)
S(1)−Sn(1)−S(3)	115.6(1)	S(2)−Sn(1)−S(4)	114.8(1)
Al(1)−Sn(1)−Al(2)	173.3(1)		

given in Table 1. Further details are in the Supporting Information.

Compound **3**·toluene crystallizes in the triclinic space group $P\bar{1}$, while **2**·toluene, **3**, and **4**·1.5toluene·THF crystallize in the monoclinic space group $P2_1/c$. The toluene solvated form of **3** will be, for clarity, noted as **3a** in the following text. The characteristics of **2**, **3**, and **3a** are the (μ-S)$_2$ bridges between the aluminum and tin atoms generating novel heterobimetallic sulfides. Compound **4** displays a spirocyclic arrangement with the tin atom at the center of the Al−(μ-S)$_2$−Sn−(μ-S)$_2$−Al moiety and represents the first example of a lipophilic complex of *ortho*-thiostannous acid. In the structures of compounds **2**, **3**, and **3a** (Figures 1 and 2), the AlS$_2$Sn four-membered rings are both perpendicular to the AlN$_2$C$_3$ plane of the ligand (L) as well as to the C−Sn−C planes. Consequently, the ligand plane and the C−N−C plane are parallel in **2**, **3**, and **3a**. In the structure of compound **4** (Figure 3), there are four conjoint planes: consisting of two six-membered ligand (L) planes and two four-membered AlS$_2$Sn planes, where every interfacing plane is perpendicular to its neighbors. The Sn−S bonds in **2** [2.402(1) and 2.403(1) Å] are slightly longer than those in **4** (2.378−2.397 Å), similar to those in **3** [2.395(1) and 2.413(1) Å], but shorter than those in **3a** [2.410(1) and 2.414(1) Å]. They are in the range of those reported previously (2.329−2.574 Å).[11] The Al−S−Sn angles of **2**, **3**, **3a**, and **4** are very similar: **2** (81.4° and 81.5°), **3** (81.7° and 82.4°), **3a** (82.5° and 82.5°), and **4** (81.8°, 82.2°, 82.1°, and 81.6°) (see Tables 2−4).

Conclusion

In summary, we have synthesized and characterized a new class of aluminum−sulfur derivatives from compound **1** and various tin chlorides.

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Supporting Information Available: CIF files for compounds **2**, **3**, **3a**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] See, for example: (a) Sekiguchi, A.; Izumi, R.; Lee, V. Y.; Ichinohe, M. *Organometallics* **2003**, *22*, 1483−1486. (b) Zimmermann, C.; Anson, C. E.; Weigend, F.; Clérac, R.; Dehnen, S. *Inorg. Chem*. **2005**, *44*, 5686−5695. (c) Palchik, O.; Lyer, R. G.; Liao, J. H.; Kanatzidis, M. G. *Inorg. Chem*. **2003**, *42*, 5052−5054. (d) Borisova, I. V.; Eaborn, C.; Hill, M. S.; Khrustalev, V. N.; Kuznetzova, M. G.; Smith, J. D.; Ustynyuk, Y. A.; Lunin, V. V.; Zemlyansky, N. N. *Organometallics* **2002**, *21*, 4005−4008.