Synthesis of a Hexadentate Hexameric Aluminum Imide and Its Metathesis Reactions

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Dedicated to Professor Bernt Krebs on the occasion of his 65th birthday

Keywords: Aluminum / Hydride ligands / N ligands / S ligands / Cluster compounds

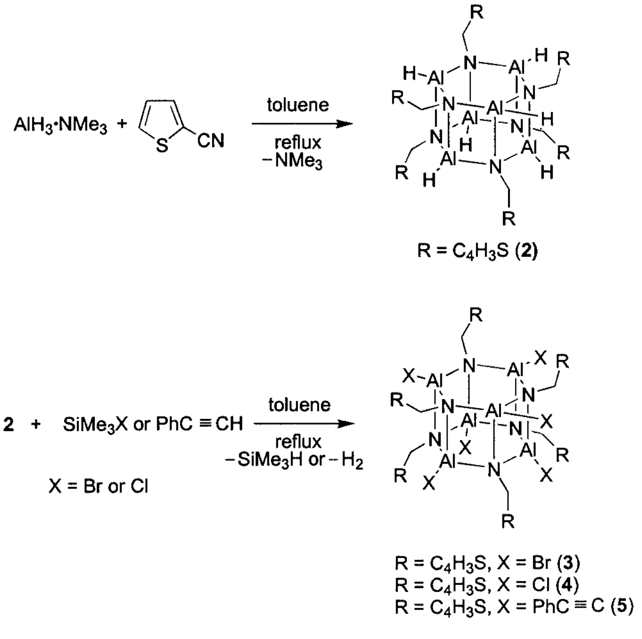
The reaction of $AlH_3{\cdot}NMe_3$ with one equivalent of 2-cyanothiophene in toluene afforded $[HAlNCH_2(C_4H_3S)]_6$ (**2**) in good yield. Treatment of **2** with $SiMe_3Br$ and $SiMe_3Cl$ in toluene under refluxing conditions resulted in the formation of compounds $[BrAlNCH_2(C_4H_3S)]_6$ (**3**) and $[ClAlNCH_2(C_4H_3S)]_6$ (**4**), respectively. In a similar way $[PhC{\equiv}CAlNCH_2(C_4H_3S)]_6$ (**5**) was readily obtained from the reaction between **2** and $PhC{\equiv}CH$. When **2** was treated with PhSH the Al-N cluster core dissociated and a four-membered ring compound $[(PhS)_2AlNHCH_2(C_4H_3S)]_2$ (**6**) was formed. In contrast, a similar hexameric aluminum imide $(HAlNCH_2Ph)_6$ (**1**) retains its Al-N network when treated with PhSH to yield $(PhSAlNCH_2Ph)_6$ (**7**). An exchange of ethyl groups and hydrides occurred when **2** was treated with excess of $ZnEt_2$, forming $[EtAlNCH_2(C_4H_3S)]_6$ **8**. Compounds **2**–**4** and **6**–**8** were characterized by X-ray single-crystal analysis.

Introduction

Recently, we have been actively involved in exploring the reactions of $AlH_3{\cdot}NMe_3$ with compounds containing C-N and C-C multiple bonds.[1] Such reactions lead to the formation of structurally interesting Al-N and Al-C clusters. In particular, a hexameric aluminum imide $(HAlNCH_2Ph)_6$ **1** can be synthesized by the treatment of PhCN with $AlH_3{\cdot}NMe_3$.[1a] We have also demonstrated that the imide **1** is stable toward certain reagents and can be functionalized easily. In our continuing efforts to synthesize functionalized aluminum imides, which can act as potential complexation agents, we have treated 2-cyanothiophene with $AlH_3{\cdot}NMe_3$. Herein we report the synthesis and metathesis reactions of an aluminum imide containing six thiophene groups, $[HAlNCH_2(C_4H_3S)]_6$ (**2**).

Results and Discussion

An interesting feature of the structure of **1** is the orientation of the benzyl groups. Three of them are aligned in one direction while the remaining three are aligned in another direction. This observation has prompted us to synthesize a hexadentate (tridentate on each side of the cluster core), hexameric aluminum imide and we have chosen 2-cyanothiophene for this purpose. Addition of a slight excess of $AlH_3{\cdot}NMe_3$ to one equivalent of 2-cyanothiophene in toluene at −78 °C and refluxing the resultant solution until the evolution of NMe_3 had ceased gave $[HAlNCH_2(C_4H_3S)]_6$ (**2**) in good yield (Scheme 1).



Scheme 1

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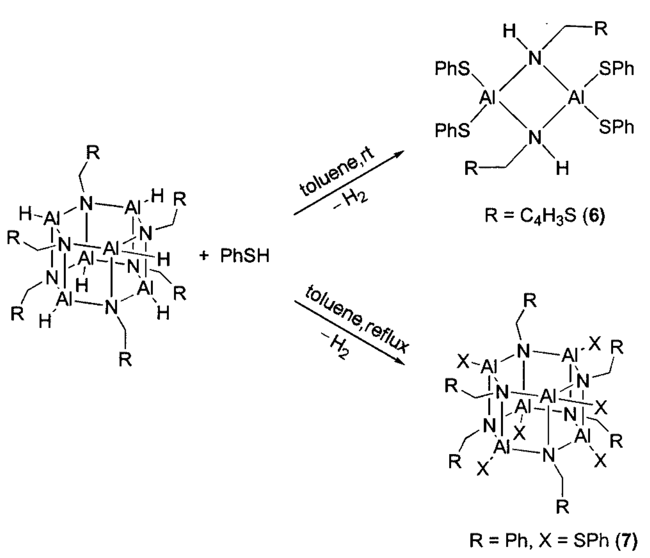
Altering the stoichiometry of the reactants decreased the yield drastically. Six thiophene groups dangling over the Al-N network make **2** hexadentate. A thorough literature search for this type of compounds was done and we found that a hexameric aluminum imide with six NMe_2 groups has been reported.[2] Treatment of **2** with $SiMe_3Br$ or $SiMe_3Cl$ in toluene under refluxing conditions resulted in the formation of compounds $[BrAlNCH_2(C_4H_3S)]_6$ (**3**) and $[ClAlNCH_2(C_4H_3S)]_6$ (**4**), respectively. In a similar way, $PhC{\equiv}CH$ reacts with **2** to give $[PhC{\equiv}CAlNCH_2(C_4H_3S)]_6$ (**5**) and evolution of H_2 (Scheme 1). Compounds **3−5** were the only isolable products of the respective reactions. In all these cases, all six hydridic hydrogens in **2** are replaced by the corresponding nucleophilic moieties and the Al-N cluster core remains intact. However, when **2** was treated with PhSH the Al-N cluster core dissociated to a four-membered ring $[(PhS)_2AlNHCH_2(C_4H_3S)]_2$ (**6**). In this reaction, migration of a proton from sulfur to nitrogen was observed (Scheme 2).



Scheme 2

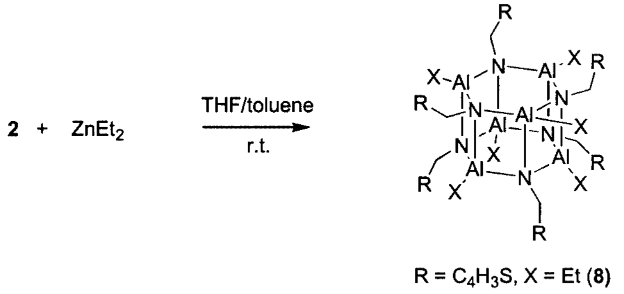
There are several four-membered Al-N rings known in the literature.[3] However, none of them carries as many as six sulfur atoms. Hence, compound **6** is the first four-membered aluminum imide carrying six sulfur atoms, of which four are connected directly to the ring aluminum atoms. To compare the stability of **2** with **1** the latter was also treated with PhSH. To our surprise, in contrast to the results of the reaction between **2** and PhSH, the Al-N network of **1** remained intact even under reflux conditions and a hexasubstituted product $(PhSAlNCH_2Ph)_6$ (**7**) was formed. The reaction between $ZnEt_2$ and **2** was also carried out in order to examine the reactivity of the Al−H bonds in **2** toward exchange reactions. Only one such example, in which $AlMe_3$ exchanges methyl groups with the hydrides of $(HAlN\textit{i}Pr)_6$,

Table 1. Crystallographic data for the structural analyses of compounds **2−4** and **6−8**

	2	**3**	**4**	**6**	**7**·$C_6H_5CH_3$	**8**
Formula	$C_{30}H_{36}Al_6N_6S_6$	$C_{30}H_{30}Al_6Br_6N_6S_6$	$C_{30}H_{30}Al_6Cl_6N_6S_6$	$C_{34}H_{32}Al_2N_2S_6$	$C_{85}H_{80}Al_6N_6S_6$	$C_{42}H_{60}Al_6N_6S_6$
Mol. wt.	834.89	1308.30	1041.54	714.94	1539.79	1003.20
T/K	133(2)	203(2)	293(2)	293(2)	133(2)	133(2)
λ/ Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Cryst system	trigonal	cubic	triclinic	monoclinic	monoclinic	cubic
Space group	$R\bar{3}$	$Pa\bar{3}$	$P\bar{1}$	$P2_1/c$	C_2/c	$Pa\bar{3}$
a (Å)	15.192(2)	16.4721(19)	10.108(2)	13.105(3)	23.525(5)	16.969(2)
b (Å)	15.192(2)	16.4721(19)	10.116(2)	9.1795(18)	14.529(3)	16.969(2)
c (Å)	14.349(3)	16.4721(19)	10.968(2)	14.822(3)	23.911(5)	16.969(2)
α (°)	90	90	98.74(3)	90	90	90
β (°)	90	90	100.97(3)	107.84(3)	111.16(3)	90
γ (°)	120	90	98.71(3)	90	90	90
V (Å^3)	2868.0(8)	4469.4(9)	1069.3(4)	1697.2(6)	7622(3)	4886.2(10)
Z	3	4	1	2	4	4
D(calcd) (g·cm^{-3})	1.450	1.944	1.617	1.399	1.342	1.364
μ(Mo-K_α) (cm^{-1})	0.528	0.5822	0.852	0.483	0.300	0.426
F(000)	1296	2544	528	744	3224	2112
θ range (°)	2.10−24.69	3.71−24.94	1.92−24.77	1.63−24.82	1.68−24.79	2.08−24.79
Index range	$-17 \leq h \leq 17$ $-17 \leq k \leq 17$ $-16 \leq l \leq 16$	$-19 \leq h \leq 19$ $-19 \leq k \leq 19$ $-1 \leq l \leq 11$	$-11 \leq h \leq 11$ $-11 \leq k \leq 11$ $-12 \leq l \leq 12$	$-15 \leq h \leq 15$ $-10 \leq k \leq 10$ $-17 \leq l \leq 17$	$-25 \leq h \leq 27$ $-17 \leq k \leq 17$ $-28 \leq l \leq 24$	$-6 \leq h \leq 18$ $-15 \leq k \leq 19$ $-19 \leq l \leq 19$
Reflns collected	6025	1968	6310	13640	21707	9292
Independent reflns	1093	1311	3342	2910	6377	1398
Refinement method	Full-matrix least-squares on F^2					
Data/restraints/parameters	1093/0/77	1311/166/101	3342/0/251	2910/0/203	6377/0/462	1398/0/91
$R1$, $R2$ $[I > 2\sigma(I)]$[a]	0.0567, 0.1698	0.0754, 0.1689	0.0443, 0.1169	0.0342, 0.0923	0.0288, 0.0742	0.0404, 0.0791
$R1$, $R2$ (all data)[a]	0.0622, 0.1773	0.1209, 0.1965	0.0535, 0.1197	0.0397, 0.0942	0.0370, 0.0763	0.0791, 0.0867
S	1.145	1.028	0.961	1.015	0.955	0.833
$\Delta\rho$(min), $\Delta\rho$(max)/e·Å^3	1.027, −0.536	0.643, −0.591	0.513, −0.545	0.552, −0.396	0.399, −0.272	0.274, −0.256

[a] $R1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$. $R2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

is known in the literature.[4] Compound **2** reacts with an excess of $ZnEt_2$ rapidly at room temperature with replacement of all its hydrides by ethyl groups, giving $[EtAlNCH_2(C_4H_3S)]_6$ (**8**; Scheme 3).[5]



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Compounds **2−4** and **6−8** were characterized by single-crystal X-ray structural analysis and the results were compared with IR, mass and elemental analysis data. A strong absorption band at 1860 cm^{-1} in the IR spectrum of **2** can be attributed to ν(Al−H).[6] The absence of this band in the IR spectra of compounds **3−6** indicates the lack of an Al−H bond in those compounds. In addition, a sharp band of strong intensity at 2129 cm^{-1} in the IR spectrum of **5** shows the presence of a C≡C moiety in the molecule.[7] Strong evidence for the presence of N−H in compound **6** comes from its IR spectrum, which contains a sharp band at 3248 cm^{-1}. The EI mass spectra of **2**, **3**, **4** and **6** exhibit the molecular ion peaks, whereas a peak related to $[M^+ - C_2H_5]$ is observed in the case of **8**. No molecular ion peak is found in the EI mass spectra of **5** and **7**.

Crystallographic data for the structural analyses of compounds **2−4** and **6−8** are given in Table 1, and important bond parameters are listed in Table 2. Compound **2** crystallizes in a trigonal space group ($R\bar{3}$) with one sixth of the molecule in the asymmetric unit. An ORTEP plot of **2** is given in Figure 1. The basic central core of the structure is comprised of an Al-N network containing six aluminum atoms and six nitrogen atoms in alternate positions, forming a hexagonal prism. Three of the six thiophenyl methyl groups dangling over one of the hexagonal faces of the polyhedron are oriented in one direction while those on the other hexagonal face are oriented in the opposite direction. The thiophene rings are oriented in such a way that the sulfur atoms are positioned slightly toward the vertical axis of the polyhedron. The bond parameters are similar to the previously studied structures and the Al−N bonds forming the hexagonal faces are significantly shorter than the transverse bonds.[1a,2,8]

Compound **3** crystallizes in the cubic space group $Pa\bar{3}$ with one sixth of the molecule in the asymmetric unit. An ORTEP plot depicting the spatial arrangement of the atoms in compound **3** is shown in Figure 2.

The sulfur atom of the thiophene group is disordered with an occupancy of 0.628(12). ORTEP plots of compounds **4** and **6−8** are given in Figures 3−6, respectively.

Table 2. Selected bond lengths and bond angles for compounds **2−4**, **6** and **7**

Bond lengths (Å)		Bond angles (deg)	
		Compound **2**	
N(1)−Al(1)	1.892(3)	N(3)−Al(3)−N(2)	115.38(15)
N(3)−Al(3)	1.894(3)	Al(1)−N(1)−Al(2)	124.33(15)
N(3)−Al(1)	1.974(3)	N(3)−Al(1)−N(1)	90.83(13)
		N(3)−Al(3)−N(1)	90.89(13)
		Al(3)−N(1)−Al(1)	89.00(12)
		Al(1)−N(3)−Al(3)	88.94(12)
		Compound **3**	
N(1)−Al(2)	1.873(8)	Al(2)−N(1)−Al(3)	124.7(4)
N(1)−Al(3)	1.876(8)	N(3)−Al(1)−N(2)	114.8(4)
N(1)−Al(1)	1.963(8)	N(3)−Al(3)−N(1)	91.3(3)
Al(1)−Br(1)	2.253(3)	N(3)−Al(1)−N(1)	91.2(3)
		Al(1)−N(3)−Al(3)	88.6(3)
		Al(3)−N(1)−Al(1)	88.5(3)
		Br(1)−Al(1)−N(1)	111.0(2)
		Br(1)−Al(1)−N(3)	119.3(3)
		Compound **4**	
N(1)−Al(2)	1.880(3)	Al(2)−N(1)−Al(3)	124.64(15)
N(1)−Al(3)	1.884(3)	N(3)−Al(1)−N(2)	115.67(12)
N(1)−Al(1)	1.972(3)	N(3)−Al(3)−N(1)	91.80(13)
Al(1)−Cl(1)	2.099(1)	N(3)−Al(1)−N(1)	91.47(12)
		Al(1)−N(3)−Al(3)	88.41(12)
		Al(3)−N(1)−Al(1)	88.42(11)
		Cl(1)−Al(1)−N(1)	112.38(9)
		Cl(1)−Al(1)−N(3)	118.75(9)
		Compound **6**	
N(1)−Al(1)	1.933(2)	Al(1)−N(1)−Al(2)	90.62(7)
N(1)−Al(2)	1.946(2)	N(1)−Al(2)−N(2)	89.38(7)
S(1)−Al(1)	2.209(1)	S(1)−Al(1)−S(2)	123.81(3)
S(2)−Al(1)	2.220(1)	S(2)−Al(1)−N(1)	104.40(6)
		S(2)−Al(1)−N(2)	110.29(6)
		Compound **7**	
N(1)−Al(1)	1.890(2)	Al(2)−N(3)−Al(3)	125.10(7)
N(3)−Al(2)	1.902(2)	N(1)−Al(1)−N(2)	115.86(6)
N(1)−Al(2)	1.975(2)	N(1)−Al(1)−N(3)	91.65(6)
N(3)−Al(1)	1.973(2)	Al(1)−N(3)−Al(3)	88.34(6)
Al(1)−S(1)	2.220(1)	S(1)−Al(1)−N(1)	117.24(5)
		S(2)−Al(2)−N(1)	120.86(4)
		S(3)−Al(3)−N(2)	111.75(5)
		Compound **8**	
N(1)−Al(2)	1.897(3)	Al(2)−N(1)−Al(3)	125.32(13)
N(1)−Al(3)	1.898(3)	N(3)−Al(1)−N(2)	114.12(14)
N(1)−Al(1)	1.987(3)	N(3)−Al(3)−N(1)	91.36(11)
Al(1)−C(1)	1.940(4)	Al(1)−N(3)−Al(3)	88.40(10)
		C(1)−Al(1)−N(1)	114.38(15)
		C(1)−Al(1)−N(2)	122.20(15)
		C(1)−Al(1)−N(3)	115.80(14)

The bond parameters and the basic structure of the Al-N network in compounds **4** and **8** are similar to those of **2**. However, the orientation of the thiophene groups in compound **8** is quite different from that in the other com-

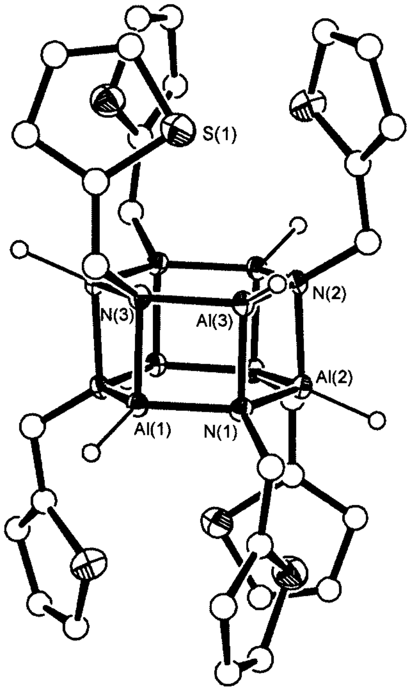


Figure 1. Crystal structure of compound [$HAlNCH_2(C_4H_3S)]_6$ (**2**); all hydrogen atoms, except those on Al, have been omitted for clarity

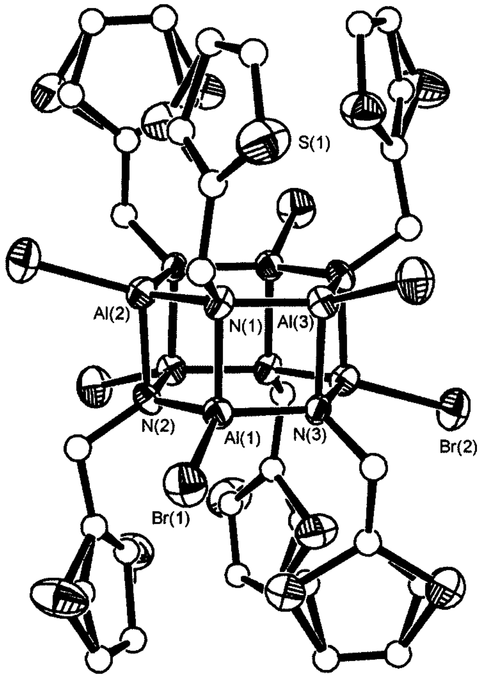


Figure 2. Crystal structure of compound [$BrAlNCH_2(C_4H_3S)]_6$ (**3**); all hydrogen atoms have been omitted for clarity

pounds. The sulfur atoms in **8** are projected away from the vertical axis, whereas they are projected toward the vertical axis in compounds **2−4**.

Compound **6** crystallizes in the cubic space group *Pa*$\bar{3}$ with half of the molecule in the asymmetric unit. Figure 4 shows the molecular structure of **6**. Two thiophenyl methyl groups are mutually *trans* and the phenyl groups on the same side of the plane of the Al-N ring are oriented in the same direction. The average Al−N bond length [1.940(2) Å] is in accordance with those reported in the literature.[3]

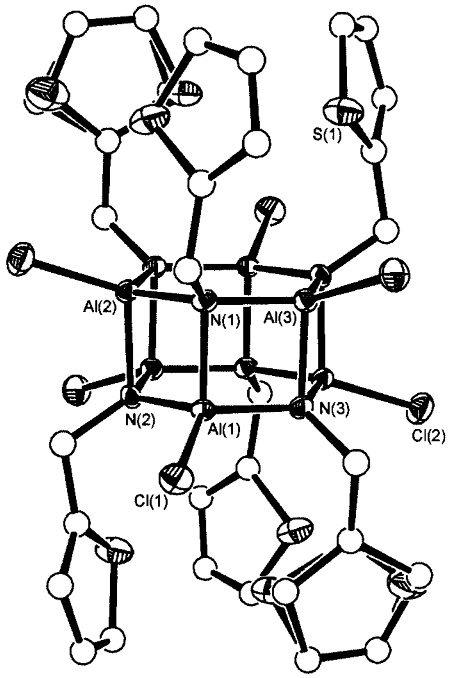


Figure 3. Crystal structure of compound [$ClAlNCH_2(C_4H_3S)]_6$ (**4**); all hydrogen atoms have been omitted for clarity

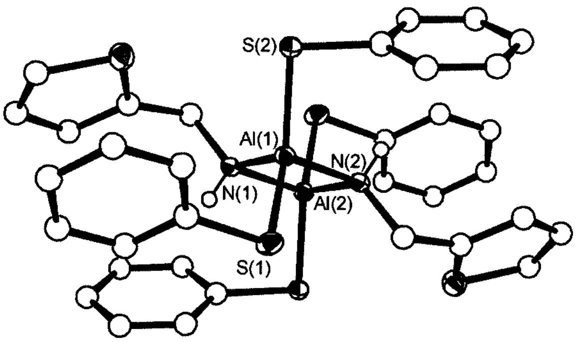
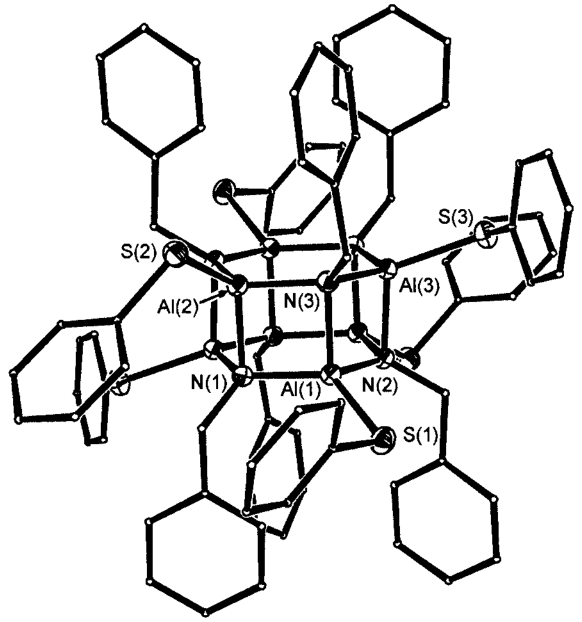


Figure 4. Crystal structure of compound [$(PhS)_2AlNHCH_2(C_4H_3S)]_2$ (**6**); all hydrogen atoms, except those on N, have been omitted for clarity

Compound **7** crystallizes in the monoclinic space group *C2/c* with half of the molecule in the asymmetric unit (Figure 5). The Al-N polyhedron is completely surrounded by organic moieties on all sides. While the bond parameters are similar to those of **1**, the bond angles between the transverse Al−N bonds and the Al−S bonds in **7** vary significantly from each other, which is not the case with compounds **3**, **4** and **8** (Figure 6; Table 2).



fiture 5. Crystal structure of compound $(PhSAlNCH_2Ph)_6$ (**7**); all hydrogen atoms have been excluded for clarity

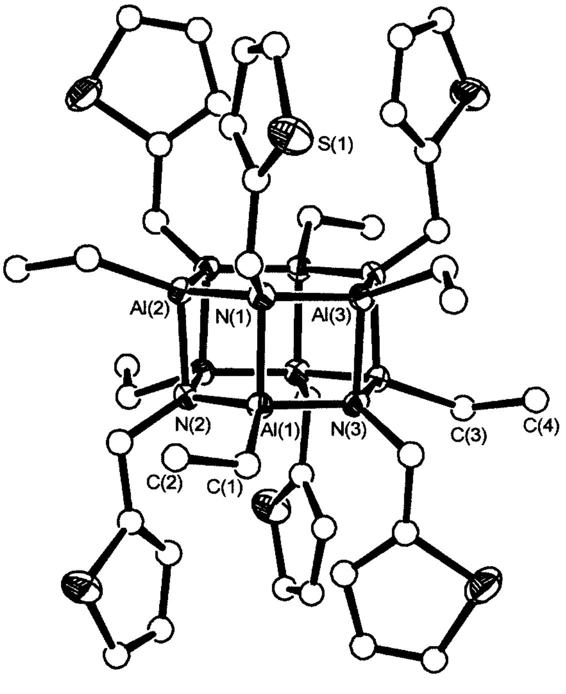


Figure 6. Crystal structure of compound $[EtAlNCH_2(C_4H_3S)]_6$ (**8**); all hydrogen atoms have been excluded for clarity

Conclusion

A hexadentate hexameric aluminum imide $[HAlNCH_2(C_4H_3S)]_6$ **2** has been synthesized and structurally characterized. Its reactivity toward reagents like $SiMe_3Br$, $SiMe_3Cl$, PhC≡CH and PhSH has been examined. We found that the Al−N network in **2** is stable toward $SiMe_3Br$, $SiMe_3Cl$ and PhC≡CH while it dissociates to form a four-membered ring with PhSH. We are currently investigating the ability of **2** and **5** to form complexes with transition metals.

Experimental Section

General Remarks: All experimental manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. The samples for spectral measurements were prepared in a dry box. Solvents were purified according to conventional procedures and were freshly distilled prior to use. $AlH_3\cdot NMe_3$ [9] and **1**[1a] were prepared as described in the literature. 2-Cyanothiophene, $SiMe_3Br$, $SiMe_3Cl$, PhSH, $ZnEt_2$ and PhC≡CH were procured from Aldrich and used as such. NMR spectra were recorded on a Bruker AM 200 instrument; chemical shifts are reported with reference to TMS. IR spectra were recorded on a Bio-Rad Digilab FTS7 spectrometer. Melting points were obtained on a HWS-SG 3000 apparatus and are uncorrected. CHN analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry at Göttingen, Germany.

Reaction of $AlH_3\cdot NMe_3$ with 2-Cyanothiophene. Synthesis of 2: $AlH_3\cdot NMe_3$ (30 mL, 0.5 M solution in toluene) was added to a solution of 2-cyanothiophene (1.50 g, 13.74 mmol) in toluene (30 mL) at −78 °C whilst stirring. The reaction mixture was allowed to warm to room temperature and then refluxed until the evolution of NMe_3 ceased. Storing the resultant solution overnight at room temperature afforded colorless crystals of **2**. Yield: 1.23 g (64%). M.p. 238−240 °C. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 4.31$ (s, 12 H, CH_2), 6.74, 6.83, 7.06 (m, 18 H, C_4H_3S) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 44.07$ (CH_2), 124.35, 125.28, 127.23, 146.95 (C_4H_3S) ppm. IR (KBr, nujol mull): $\tilde{\nu} = 1860$ (s), 1718 (w), 1648 (w), 1596 (w), 1528 (w), 1339 (m), 1269 (m), 1216 (m), 1156 (m), 1075 (w), 1040 (w), 1013 (w), 969 (w), 854 (s), 819 (s), 753 (w), 723 (w), 693 (w), 658 (w), 637 (w), 621 (w), 529 (m), 481 (m), 438 (m), 413 (w) cm^{-1}. EI-MS: *m/z* (%) = 834 (20) $[M^+]$, 737 (28) $[M^+ - CH_2C_4H_3S]$, 653 (36) $[M^+ - (CH_2C_4H_3S + C_4H_4S)]$, 113 (100) $[H_2NCH_2C_4H_3S^+]$. $C_{30}H_{36}Al_6N_6S_6$ (834.89): calcd. C 43.16, H 4.35, N 10.07; found C 43.23, H 4.46, N 9.35.

Reaction of 2 with $SiMe_3Br$. Synthesis of 3: $SiMe_3Br$ (1.07 g, 6.99 mmol) was added at room temperature to a suspension of **2** (0.73 g, 0.87 mmol) in toluene (30 mL). The reaction mixture was stirred overnight at room temperature and refluxed for an hour. The solution was filtered and cooled to room temperature to obtain colorless crystals of **3**. Yield: 0.77 g (68%). M.p. 284−287 °C. IR (KBr, nujol mull): $\tilde{\nu} = 1887$ (m), 1780 (w), 1714 (w), 1647 (w), 1602 (w), 1532 (w), 1433 (m), 1335 (s), 1272 (s), 1226 (m), 1216 (m), 1162 (s), 1135 (w), 1074 (w), 1043 (w), 977 (w), 891 (w), 850 (s), 826 (s), 757 (w), 723 (w), 655 (m), 617 (m), 562 (s), 520 (m), 504 (s), 465 (m), 435 (s) cm^{-1}. EI-MS: *m/z* (%) = 1308 (5) $[M^+]$, 179 (100), 113 (16) $[H_2NCH_2C_4H_3S^+]$. $C_{30}H_{30}Al_6Br_6N_6S_6$ (1308.30): calcd. C 27.54, H 2.31, N 6.42; found C 27.15, H 2.85, N 6.19.

Reaction of 2 with $SiMe_3Cl$. Synthesis of 4: The reaction between **2** (0.50 g, 0.60 mmol) and $SiMe_3Cl$ (0.45 g, 4.14 mmol) was carried out in a similar manner to that between **2** and $SiMe_3Br$. Yield: 0.44 g (71%). M.p. 218−223 °C. IR (NaCl, nujol mull): $\tilde{\nu} = 1889$ (w), 1797 (w), 1724 (w), 1650 (w), 1594 (w), 1531 (w) 1495 (w), 1435 (m), 1341 (s), 1272 (s), 1219 (s), 1158 (s), 1135 (w), 1074 (w), 1042 (w), 972 (w), 896 (w), 855 (s), 824 (s), 753 (w), 728 (w), 685 (w), 653 (w), 622 (m), 593 (m), 564 (w), 540 (w) cm^{-1}. EI-MS:

m/z (%) = 1040 (10) [M^+], 943 (10) [$M^+ - CH_2C_4H_3S$], 97 (100) [$CH_2C_4H_3S^+$]. $C_{30}H_{30}Al_6Cl_6N_6S_6$ (1041.54): calcd. C 34.59, H 2.90, N 8.07; found C 33.57, H 3.47, N 7.64.

Reaction of 2 with PhC≡CH. Synthesis of 5: PhC≡CH (0.42 g, 4.11 mmol) was added at room temperature to a suspension of **2** (0.50 g, 0.60 mmol) in toluene (30 mL). The reaction mixture was stirred for half an hour at room temperature before refluxing it until the evolution of H_2 ceased. The resultant dark brown solution was filtered and kept for crystallisation at room temperature. Yield: 0.55 g (64%). M.p. 270 °C (decomp). ^1H NMR (200 MHz, $CDCl_3$): δ = 4.68 (s, 12 H, CH_2), 6.79, 6.95, 7.04 (m, 18 H, C_4H_3S), 7.27 (m, 18 H, *m*- and *p*-C_6H_5), 7.46 (m, 12 H, *o*-C_6H_5) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 41.28 (CH_2), 67.98 (Al − C), 83.15 (Al − C≡C), 122.14, 128.30, 128.77, 132.14 (C_6H_5), 125.30, 128.23, 129.04, 137.88 (C_4H_3S) ppm. IR (NaCl, nujol mull): ṽ = 2129 (s), 2030 (w), 1951 (w), 1880 (w), 1801 (w), 1675 (w), 1653 (w), 1594 (w), 1572 (w), 1540 (w), 1486 (m), 1341 (w), 1276 (w), 1214 (s), 1175 (w), 1156 (m), 1098 (w), 1068 (w), 1044 (w), 1025 (w), 996 (w), 971 (w), 915 (w), 894 (w), 851 (m), 817 (m), 799 (w), 755 (m), 726 (w), 690 (w), 647 (w), 610 (w), 565 (w), 535 (w) cm^{-1}. In the EI-MS spectrum only low molecular weight fragments were found. $C_{78}H_{60}Al_6N_6S_6$ (1434.21): calcd. C 65.26, H 4.21, N 5.85; found C 64.93, H 4.76, N 5.77.

Reaction of 2 with PhSH. Synthesis of 6: PhSH (0.46 g, 4.17 mmol) was added slowly at room temperature to a suspension of **2** (0.50 g, 0.60 mmol) in toluene (30 mL). Evolution of H_2 was observed during the addition. The reaction mixture was stirred overnight and filtered. Colorless crystals of **6** were obtained when the filtrate was stored at room temperature. Yield: 0.63 g (84% based on PhSH). M.p. 143−153 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.80 (s, 2 H, NH), 3.90 (s, 4 H, CH_2), 6.42, 6.82 (m, 4 H, C_4H_3S), 7.21 (m, 14 H, C_6H_5S, C_4H_3S), 7.55 (m, 8 H, C_6H_5S) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 41.38 (CH_2), 123.95, 125.63, 127.17, 137.07 (C_4H_3S), 125.63, 129.07, 129.46, 130.74 (C_6H_5S) ppm. IR (KBr, nujol mull): ṽ = 3248 (m), 3231 (w), 3160 (w), 1954 (w), 1882 (w), 1655 (w), 1579 (m), 1473 (m), 1436 (m), 1380 (m), 1326 (w), 1303 (w), 1257 (m), 1205 (m), 1147 (w), 1082 (m), 1066 (w), 1043 (w), 1023 (m), 971 (s), 907 (w), 864 (s), 828 (m), 740 (s), 709 (m), 691 (s), 647 (m), 574 (m), 554 (m), 530 (s), 492 (w), 483 (w), 472 (s) cm^{-1}. EI-MS: *m/z* (%) = 714 (5) [M^+], 605 (68) [$M^+ - PhSH$], 110 (100) [$PhSH^+$]. $C_{34}H_{32}Al_2N_2S_6$ (714.94): calcd. C 57.12, H 4.51, N 3.92; found C 56.76, H 4.63, N 3.74.

Reaction of 1 with PhSH. Synthesis of 7: PhSH (0.50 g, 4.54 mmol) was added at room temperature to a suspension of **1** (0.52 g, 0.65 mmol) in toluene (30 mL). The reaction mixture was stirred for an hour at room temperature before refluxing it until the evolution of H_2 ceased. The solution was filtered and kept for crystallisation at room temperature. Yield: 0.66 g (70%). ^1H NMR (200 MHz, $CDCl_3$): δ = 4.22 (s, 12 H, CH_2), 6.95 (m, 24 H, *o*-$CH_2C_6H_5$ and *o*-SC_6H_5), 7.22 (m, 36 H, *m*-, *p*-$CH_2C_6H_5$ and *m*-, *p*-SC_6H_5) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.70 (CH_2), 126.97 (*p*-$CH_2C_6H_5$), 127.16 (*m*-$CH_2C_6H_5$), 127.56 (*o*-$CH_2C_6H_5$), 137.06 (CH_2-*C*), 128.49 (*p*-SC_6H_5), 128.59 (*m*-SC_6H_5), 129.06 (*o*-SC_6H_5), 130.74 (S-C) ppm. IR (KBr, nujol mull): ṽ = 1579 (m), 1496 (m), 1437 (w), 1367 (w), 1300 (w), 1282 (w), 1260 (w), 1198 (w), 1156 (w), 1079 (w), 1066 (w), 1031 (w), 1023 (w), 1003 (w), 974 (w), 810 (w), 735 (s), 693 (w), 667 (w), 547 (s), 524 (m), 480 (s), 459 (w), 439 (w) cm^{-1}. $C_{85}H_{80}Al_6N_6S_6$ (**7**·$C_6H_5CH_3$) (1539.79): calcd. C 66.30, H 5.24, N 5.46; found C 66.67, H 5.35, N 5.16. In the EI-MS spectrum only low molecular weight fragments were found.

Reaction of 2 with $ZnEt_2$. Synthesis of 8: A solution of $ZnEt_2$ (15 mL, 1.1 M solution) in toluene was added dropwise to a solution of **2** (0.85 g, 1.02 mmol) in THF (20 mL). The resultant mixture was stirred overnight at room temperature and then filtered. The filtrate was reduced in volume to 15 mL and stored at 0 °C to obtain colorless crystals of **8**. Yield: 0.81 g (79%). M.p. 262 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.20 (m, 12 H, $AlCH_2$), 1.11 (t, 18 H, CH_3), 4.38 (s, 12 H, NCH_2), 6.65, 6.79, 7.09 (m, 18 H, C_4H_3S) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = −1.09 (Al-CH_2), 9.81 (CH_3), 43.45 (NCH_2), 123.63, 124.88, 126.72, 147.37 (C_4H_3S) ppm. IR (NaCl, nujol mull): ṽ = 1337 (m), 1269 (m), 1225 (s), 1199 (w), 1157 (w), 1125 (w), 1072 (w), 1006 (s), 990 (s), 973 (s), 927 (s), 848 (s), 823 (s), 767 (s), 717 (s), 696 (s), 636 (s) cm^{-1}. EI-MS: *m/z* (%) = 974 (45) [$M^+ - C_2H_5$], 973 (100) [$M^+ - C_2H_6$]. $C_{42}H_{60}Al_6N_6S_6$ (1003.20): calcd. C 50.28, H 6.03, N 8.38; found C 50.56, H 6.03, N 8.02.

X-ray Structure Determination of 2−4, 6 and 7: A suitable crystal of each compound was mounted on a glass fiber and coated with paraffin oil. Diffraction data for **3** were collected on a Siemens−Stoe AED2 four-circle instrument, and for **2**, **4**, **6**, **7** and **8** the data were collected on a STOE IPDS II diffractometer. All measurements were made with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS-97[10] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[11] All non-hydrogen atoms were refined anisotropically. Neutral-atom scattering factors (including anomalous scattering) were taken from International Tables for X-ray Crystallography.[12] Hydrogen atoms were included at geometrically calculated positions and refined using a riding model.

CCDC-192059 to -192063 and CCDC-192424 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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