Low-Temperature Synthesis of Aluminum Sulfide as the Solvate Al$_4$S$_6$(NMe$_3$)$_4$ in Hydrocarbon Solution
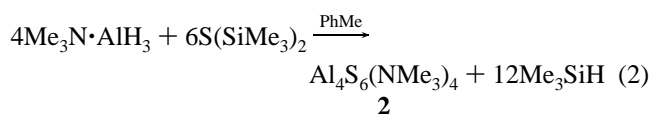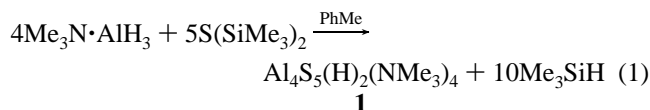
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Aluminum sulfide, Al$_2$S$_3$, a moisture-sensitive colorless solid, has a variety of structures in the crystalline phase[1] and is synthesized by the direct reaction of the elements at elevated temperature. The moisture sensitivity and the high-temperature synthesis are features common to most binary heavier main group 13–15 and 13–16 compounds.[2] Their high lattice energy,[3] however, precludes solubility at ambient temperature in media with which they do not react. The isolation and purification of stoichiometric neutral cage fragments of such lattices under mild conditions is thus an important synthetic challenge, since many binary group 13–15 and 13–16 compounds have interesting electronic properties.[4] One approach to the problem involves the generation of such substances by a homogeneous reaction in solution followed by their stabilization and crystallization as a complex with neutral donor ligands. Some neutral lithium halide fragments have been synthesized by this method.[5] This general approach has also been applied to a number of cages of the heavier chalcogenides such as Cu$_{50}$S$_{25}${P(tBu)$_2$Me}$_{16}$[6a] and Cu$_{146}$Se$_{73}$(PPh$_3$)$_{30}$.[6b] To date, however, it has not proven possible to synthesize cage complexes in which both the metal ion and counteranion have high formal charges as in group 13–15 or 13–16 binary species.[7] It is now shown that the reaction between Me$_3$N·AlH$_3$ and S(SiMe$_3$)$_2$ at relatively low temperature leads to the aluminum sulfide complexes Al$_4$S$_5$(H)$_2$(NMe$_3$)$_4$·PhMe (1·PhMe) and Al$_4$S$_6$-(NMe$_3$)$_4$ (2) in moderate yields.

The preparative routes to **1** and **2** involve the stoichiometries given in eqs 1 and 2. The use of S(SiMe$_3$)$_2$ as the chalcogenide

$$4Me_3N\cdot AlH_3 + 5S(SiMe_3)_2 \xrightarrow{PhMe}$$
$$Al_4S_5(H)_2(NMe_3)_4 + 10Me_3SiH \quad (1)$$
$$\mathbf{1}$$

$$4Me_3N\cdot AlH_3 + 6S(SiMe_3)_2 \xrightarrow{PhMe}$$
$$Al_4S_6(NMe_3)_4 + 12Me_3SiH \quad (2)$$
$$\mathbf{2}$$

transfer agent was prompted by the reaction of the alane (Mes*AlH$_2$)$_2$ (Mes* = -C$_6$H$_2$-2,4,6-(tBu)$_3$) with the siloxane (Me$_2$SiO)$_3$ to afford the alumoxane (Mes*AlO)$_4$ in high yield with

elimination of Me$_2$SiH$_2$.[8] In addition, direct interaction of the elemental chalcogens Se and Te with Me$_3$N·AlH$_3$ has been shown to afford {Me$_3$N·Al(H)(μ_2-E)}$_2$ (E = Se or Te).[9]

Reaction of Me$_3$N·AlH$_3$ and S(SiMe$_3$)$_2$ in toluene at 90–95 °C according to eq 1 affords **1**·PhMe in 67% purified yield.[10a] X-ray data[11a] show that its structure (Figure 1) is a bicyclic Al$_4$S$_5$ [3.3.1] array in which two fused six-membered AlS rings have a boat conformation. Each Al is bound to a Me$_3$N donor (av Al−N = 2.021(7) Å) as well as to two μ_2-sulfides (av Al−S = 2.223(11) Å). In addition, the two bridgehead Al atoms (Al(1) and Al(3)) are linked by a μ_2-sulfide (av Al−S = 2.232(2) Å), whereas Al(2) and Al(4) each carry a hydrogen (av Al−H = 1.54(5) Å). Thus, all aluminums in **1**·PhMe have distorted tetrahedral coordination. Spectroscopic data (^{1}H, ^{13}C, and ^{27}Al NMR and IR) are in harmony with the formula established for **1**·PhMe by X-ray crystallography. ^{1}H NMR spectroscopy reveals a 1:1 ratio of **1** and PhMe and a 2:1 ratio of Me$_3$N and Al−H groups. IR absorptions for the Al−H and Al−S bonds were observed at 1782 and 503 cm^{-1}.

Complete elimination of Al hydrogen is observed in the reaction of Me$_3$N·AlH$_3$ with a slight excess of S(SiMe$_3$)$_2$ over the required stoichiometry (i.e., >1.5 S per Al).[10b] The structure of the product Al$_4$S$_6$(NMe$_3$)$_4$ (**2**)[11b] features an adamantanyl Al$_4$S$_6$ framework with each bridgehead Al complexed to Me$_3$N (Al−N = 1.991(4) Å) and three μ_2-sulfides (Al−S = 2.2235-(7) Å) (Figure 2). The coordination at the aluminums is thus distorted tetrahedral (S−Al−S = 114.61(2)°, S−Al−N = 103.65(3)°), and the two-coordinate sulfurs feature an Al−S−Al angle of 97.82(6)°. Attempts to convert **1** to **2** via reaction of 1 equiv of S(SiMe$_3$)$_2$ have been only partially successful. The major problem arose from attempted redissolution of **1**·PhMe in PhMe which results in the deposition of an (as yet

(7) However, related cage species (e.g., Cd$_{32}$Se$_{14}$(SePh)$_{36}$(PPh$_3$)$_4$ or Cu$_{96}$P$_{30}${P(SiMe$_3$)$_6$(PEt$_3$)$_{18}$} having multiply-charged anionic ligands have been synthesized. See: Behrens, S.; Bettenhausen, M.; Deveson, A. C.; Eichhofer, A.; Fenske, D.; Lohde, A.; Woggon, U. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2215. Fenske, D.; Holstein, W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1290.

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(10) All manipulations were carried out under anaerobic and anhydrous conditions. Both **1** and **2** gave satisfactory C, H, and N elemental analyses. (a) Al$_4$S$_5$(H)$_2$(NMe$_3$)$_4$·PhMe (**1**·PhMe). A solution of 0.36 g (4.0 mmol) of H$_3$AlNMe$_3$[10c] in toluene (25 mL) was treated with 1.06 mL (5.0 mmol) of (Me$_3$Si)$_2$S[10d] at room temperature and heated to 90−95 °C for 24 h. The small amount of voluminous, grayish precipitate was separated, and the clear, colorless supernatant liquid was concentrated to *ca*. 3 mL and cooled in a −20 °C freezer for 3 days to afford 0.40 g of colorless crystals of **1**·PhMe. Recrystallization from toluene (20 mL) gave 0.16 g of the pure product as colorless crystals of sufficient quality for X-ray crystallography. Yield: 27%. The crystals turn opaque at mp = 75−90 °C (desolvation), foams at *ca*. 250 °C, and do not melt below 315 °C. ^{1}H NMR (C$_6$D$_6$): 7.05 (m, toluene, 5H), 4.9 (s, br, $w_{1/2}$ = 170 Hz, Al−H, 2H), 2.47 (s, Me$_3$N, 18H), 2.29 (s, Me$_3$N, 18H), 2.10 (s, toluene, 3H). ^{13}C{^{1}H} NMR (C$_6$D$_6$): 47.2 (Me$_3$N). ^{27}Al NMR (C$_6$D$_6$, ν_o = 78.34047 MHz): 146 (s, $w_{1/2}$ ≈ 1900 Hz). IR (Nujol mull): 1782 (st, Al−H). (b) Al$_4$S$_6$(NMe$_3$)$_4$, **2**. (Me$_3$Si)$_2$S (1.27 mL, 6.0 mmol) was added to a solution of H$_3$AlNMe$_3$ (0.36 g, 4.0 mmol) in toluene (25 mL), and the mixture was heated to 110−115 °C for *ca*. 17 h. The clear, colorless solution was separated from the small amount of voluminous precipitate and heated to 110−115 °C for an additional 4 d to afford a colorless, crystalline solid, which was washed with *n*-pentane (20 mL) and dried under reduced pressure. This solid consists of at least two different compounds: bundles of thin plates or needles which still contain the Al−H function (by IR) and clear blocks of approximately cubo-octahedral shape with a maximum size of 0.2 mm in an estimated 60:40 ratio. The blocks were of sufficient quality for X-ray diffraction. Yield: 0.26 g. This compound does not melt below 315 °C. (c) Ruff, J. K.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1960**, *82*, 2141. (d) Armitage, D. A.; Clark, M. J.; Sinden, A. W.; Wingfield, J. N.; Abel, E.W.; Louis, E. J. *Inorg. Synth.* **1974**, *15*, 207.

(11) Crystal data at 130 K with Cu Kα (λ = 1.541 78 Å) radiation: (a) **1**·PhMe, C$_{19}$H$_{46}$Al$_4$N$_4$S$_5$, M_r = 598.82, orthorhombic, space group *Pna*2$_1$, a = 11.8936(12) Å, b = 27.252(2) Å, c = 10.042(2) Å, V = 3255.0(7) Å^3, D_{calcd} = 1.222 g cm^{-3}, Z = 4, R = 0.0253 for 2189 (I > 2σ(I)) reflections; (b) Al$_4$S$_6$(NMe$_3$)$_4$ (**2**), C$_{12}$H$_{36}$Al$_4$N$_4$S$_6$, M_r = 536.73, cubic, space group *I*43*m*, a = 11.4095(9) Å, V = 1485.3(2) Å^3, D_{calcd} = 1.200 g cm^{-3}, Z = 2, R = 0.0305 for 172 (I > 2σ(I)) reflections.

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(3) The lattice energy for an ionic compound may be estimated by using the Kapustinskii equation. This shows that the lattice energies of species such as Al$_2$S$_3$ with multiply-charged ions are often more than an order of magnitude greater than that the simplest ionic species such as NaCl. Kapustinskii, A. F. *Z. Phys. Chem.* (*Leipzig*) **1933**, *B22*, 257.

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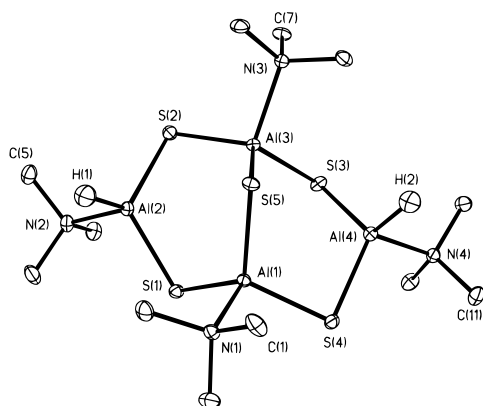
Figure 1. Thermal ellipsoidal (30%) plot of **1**. Hydrogen atoms are not shown except for H(1) and H(2). Selected bond distances (Å) and angles (deg) are the following: Al(1)−S(1) = 2.208(2), Al(1)−S(4) = 2.221(2), Al(1)−S(5) = 2.230(2), Al(2)−S(1) = 2.232(2), Al(2)−S(2) = 2.229(2), Al(3)−S(2) = 2.214(2), Al(3)−S(3) = 2.202(2), Al-(3)−S(5) = 2.233(2), Al(4)−S(3) = 2.225(2), Al(4)−S(4) = 2.235(2), Al(1)−N(1) = 2.032(2), Al(2)−N(2) = 2.022(4), Al(3)−N(3) = 2.017-(4), Al(4)−N(4) = 2.013(3), Al(2)−H(1) = 1.58(4), Al(4)−H(2) = 1.51(5), Al(1)−S(1)−Al(2) = 99.50(6), Al(1)−S(5)−Al(3) = 96.35-(5), S(1)−Al(1)−S(4) = 115.37(6), S(1)−Al(1)−S(5) = 114.22(6), S(4)−Al(1)−S(5) = 114.06(6), S(1)−Al(1)−N(1) = 104.76(11), S(4)−Al(1)−N(1) = 103.97(11).
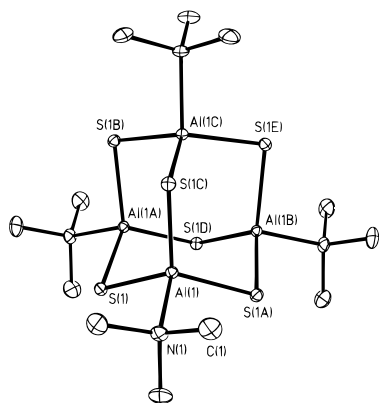

Figure 2. Thermal ellipsoidal (30%) plot of **2**. Hydrogen atoms are not shown. Selected bond distances (Å) and angles (deg) are the following: Al(1)−S(1) = 2.2235(7), Al(1)−N(1) = 1.991(4), Al(1)−S(1)−Al(1a) = 97.82(6), S(1)−Al(1)−S(1a) = 114.61(2), S(1)−Al-(1)−N(1) = 103.65(3).

unidentified) insoluble solid but having both Al−H and Al−S IR absorptions.

The Al−N and Al−S structural parameters in **1** and **2** are consistent with currently available data on related complexes. For example, the Al−N distances in **1** (2.032(7) Å) and **2** (1.991-(4) Å) may be compared to the 2.011(9) Å observed in {Me₃-

NAl(H)(μ₂-E)}₂ (E = Se or Te).⁹ The Al−S distances in **1** and **2** (ca. 2.22 Å) are shorter than those in the recently reported {(Me₂EtC)AlS}₄¹² (ca. 2.31 Å) which involves μ₃-S sulfides in an Al₄S₄ cubane arrangement, but are longer than those in S[Al{CH(SiMe₃)₂}₂]₂ (Al−S = 2.187(4) Å)¹³ or Al(SMes*)₃ (av Al−S = 2.185(5) Å)¹⁴ where, although the sulfide or thiolate has a two-coordinate S, the Al is three-coordinate. The closest known structure to **2** is the adamantanyl species Al₄I₄(SMe)₄S₂¹⁵ in which four of the six core sulfurs are derived from thiolates. The Al−μ₂-S (sulfide) distances average 2.18(2) Å which, owing to the higher standard deviations, cannot be regarded as appreciably shorter than the Al−S bond length in **2**. The ternary compound TlAlS₂ has also been described as isomorphous to TlGaSe₂,¹⁶ which consists of layers of corner-sharing adaman-tane-like [M₄X₁₀] (M = Al, Ga, In; X = S, Se)¹⁷ supertetrahedra, but no additional details were given.

Although the stoichiometry of the Al₄S₆ core in **2** corresponds to the formula of Al₂S₃, the coordination of the Al in **2** involves three sulfides and one amine nitrogen. It thus differs from the essentially tetrahedral AlS₄ environment found in Al₂S₃¹⁸ and the related anionic salts TlAlS₂,¹⁶ᵃ Tl₃Al₇S₁₂,¹⁹ and Tl₃Al₁₃S₂₁,¹⁶ᵇ whose structures consist of corner-sharing Al-centered AlS₄ tetrahedra. Nonetheless, the adamantanyl core of **2** is composed of S₃AlN tetrahedra in which the sulfide corners are also shared. Thus, **2** is the smallest neutral unit with the correct Al₂S₃ stoichiometry which resembles the structure of Al₂S₃. A putatively smaller neutral Al₂S₃(NMe₃)₂ fragment would prob-ably be different in the sense that its structure would consist of an Al₂S₃ trigonal bipyramid with face- rather than corner sharing-NAlS₃ tetrahedra. Attempted sublimation of **2** at low pressure and ca. 250 °C results in the elimination of NMe₃ and the deposition of an amorphous form of Al₂S₃.

Supporting Information Available: Tables of data collection parameters, atom coordinates, bond distances, angles, anisotropic thermal parameters, and hydrogen coordinates (21 pages). See any current masthead page for ordering and Internet access instructions.

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