

# New route to organoaluminium sulfides: synthesis of $(\text{Mes}^*\text{AlS})_2$ ( $\text{Mes}^* = -\text{C}_6\text{H}_2\text{Bu}^t_{3-2,4,6}$ ) and its dimethyl sulfoxide adduct $[\text{Mes}^*\text{AlS}(\text{OSMe}_2)]_2$

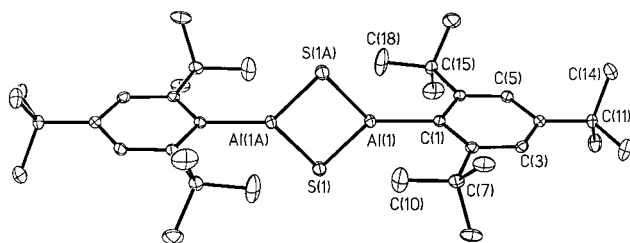
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Treatment of the alane  $(\text{Mes}^*\text{AlH}_2)_2$  ( $\text{Mes}^* = -\text{C}_6\text{H}_2\text{Bu}^t_{3-2,4,6}$ ) with  $\text{S}(\text{SiMe}_3)_2$  in refluxing toluene affords the novel organoaluminium sulfide  $(\text{Mes}^*\text{AlS})_2$  **1** which has a previously unobserved dimeric structure; treatment of **1** with 2 equiv. of  $\text{Me}_2\text{SO}$  furnishes the complex  $[\text{Mes}^*\text{AlS}(\text{OSMe}_2)]_2$  **2** in which a dimeric configuration is retained, and which shows weak intermolecular interactions between neighboring dimers.

Group 13 organometallic chalcogenide species of formula  $(\text{RME})_n$  ( $\text{R} = \text{alkyl, aryl}$ ;  $\text{M} = \text{Al, Ga, In}$ ;  $\text{E} = \text{O-Te}$ ) are usually synthesized with use of the organometallic precursors  $\text{MR}_3$ .<sup>1</sup> For the heavier chalcogenide derivatives, direct interaction of the elements themselves (*i.e.* S, Se, Te) with the metal trialkyls has afforded several new compounds which have three-dimensional cage structures.<sup>2</sup> For the lighter oxide derivatives, however, the reaction between water (or water complexed in metal salts)<sup>3</sup> remains the preferred method of synthesis of  $(\text{RMO})_n$  compounds.† Recently, it has been shown that aluminium hydride compounds are also useful precursors for the synthesis of organoalumoxanes.<sup>4</sup> Thus, the reaction of the hydride  $(\text{Mes}^*\text{AlH}_2)_2$ <sup>5</sup> ( $\text{Mes}^* = -\text{C}_6\text{H}_2\text{Bu}^t_{3-2,4,6}$ ) with  $(\text{Me}_2\text{SiO})_3$  affords the unique tetramer  $(\text{Mes}^*\text{AlO})_4$  with elimination of  $\text{SiH}_2\text{Me}_2$ . We now report that the reaction of  $(\text{Mes}^*\text{AlH}_2)_2$  with  $\text{S}(\text{SiMe}_3)_2$ ‡ affords the unique, dimeric, heavier chalcogenide derivative  $(\text{Mes}^*\text{AlS})_2$  **1** and that treatment of **1** with  $\text{Me}_2\text{SO}$  does not effect dissociation of the dimeric structure but affords the adduct  $[\text{Mes}^*\text{AlS}(\text{OSMe}_2)]_2$ , **2**.

Compound **1**, which displays high thermal stability ( $\text{mp} > 200^\circ\text{C}$ ), can be synthesized§ in almost quantitative yield by refluxing  $(\text{Mes}^*\text{AlH}_2)_2$  with 2 equiv. of  $\text{S}(\text{SiMe}_3)_2$  in either toluene or *n*-octane. X-Ray crystallographic data¶ for **1** show that it crystallizes as dimeric units (Fig. 1) which have a crystallographically required inversion center. The planar  $\text{Al}_2\text{S}_2$  core is characterized by almost equal Al–S distances of 2.2083(9) and 2.2107(14) Å and internal ring angles of 78.09(3)° at S and 101.91(3)° at Al. The external S–Al–C angles, 127.94(7) and 130.14(7)°, are quite similar, so that the sum of the angles at Al is 359.99° indicating strictly planar coordination at Al. However, there are also short (2.26–2.33 Å) interactions between a number of *ortho*-Bu<sup>t</sup> H atoms and Al.



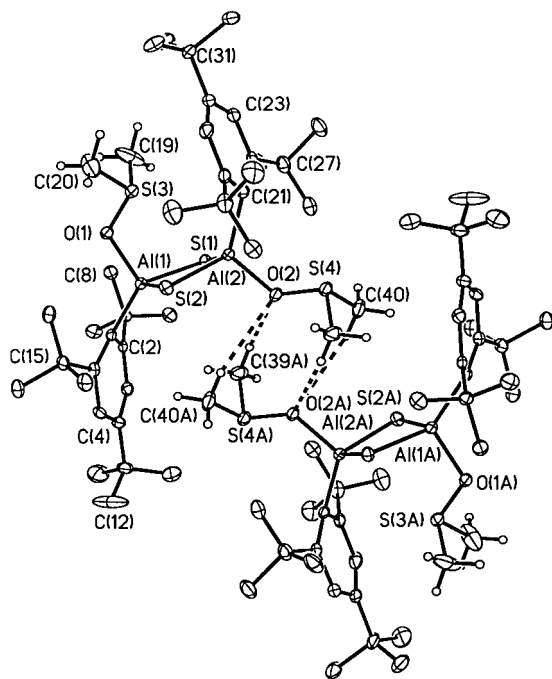
**Fig. 1** Thermal ellipsoidal (30%) plot of **1** with H atoms not shown. Some important bond distances (Å) and angles (°): Al(1)–S(1) 2.2083(9), Al(1)–S(1A) 2.2107(14), Al–C(1) 1.956(2), Al(1)⋯Al(1A) 2.7835(13); Al(1)–S(1)–Al(1A) 78.09(3), S(1)–Al(1)–S(1A) 101.91(3), S(1)–Al(1)–C(1) 127.94(7), S(1A)–Al(1)–C(1) 130.14(7).

The angle between the normals to the  $(\text{AlS})_2$  and aromatic ring planes is 89.3°.

The dimeric structure of **1** may be contrasted with the tetrameric structure of the corresponding oxide species  $(\text{Mes}^*\text{AlO})_4$ <sup>4</sup> which features an almost planar, eight-membered  $\text{Al}_4\text{O}_4$  ring with wide (*ca.* 151°) Al–O–Al angles. The lower aggregation in **1** thus, may be a consequence of the reluctance of the S atoms to hybridize which imposes a narrower interbond angle. This leads to greater steric congestion in the molecule which results in the lower degree of aggregation observed for **1**. Apparently, **1** is only the second example of a mono-organoaluminium sulfide to be fully structurally characterized. The only previous example is the tetrameric species  $[(\text{Me}_2\text{Et-C})\text{AlS}]_4$ <sup>2d</sup> which has an  $\text{Al}_4\text{S}_4$  cubane structure with Al–S distances in the range 2.295(8)–2.319(9) Å. The longer Al–S distances in that compound are due to the higher coordination numbers of both Al (four) and S (three). The short Al–S distances in **1** are similar to those observed in the low-coordinate compounds  $\text{Al}(\text{SMes}^*)_3$ <sup>6</sup> [Al–S 2.172(2)–2.191(2) Å],  $\text{S}[\text{Al}\{\text{CH}(\text{SiMe}_3)_2\}]_2$ <sup>7</sup> [Al–S 2.187(4) Å] and  $\text{Al}_4\text{I}_4\text{S}_2(\text{SMe})_4$ <sup>8</sup> [Al–S (two-coordinate) 2.16(1)–2.20(1) Å].

The dimethyl sulfoxide adduct **2** was prepared by the addition of 2 equiv. of  $\text{Me}_2\text{SO}$  to **1** in benzene. Complex **2** was formed essentially instantaneously and it is precipitated from benzene at room temperature. Heating the solution to reflux temperature resulted in redissolution of the precipitate and cooling slowly resulted in crystals suitable for X-ray crystallography. The X-ray data for **2** show that the dimeric  $\text{Al}_2\text{S}_2$  core structure (Fig. 2) remains intact and that the metals are each complexed by one dimethyl sulfoxide molecule which are disposed on opposite sides of the  $\text{Al}_2\text{S}_2$  core. This results in an increase of *ca.* 0.05 Å in the Al–S bond lengths which span the narrow range 2.243(2)–2.259(2) Å. The Al–C distances are lengthened by about the same amount; from 1.956(2) Å in **1** to an average of 2.022(8) Å in **2**. The average Al–O distance is 1.86(1) Å, which is within the range found in related complexes.<sup>9</sup> Also, the  $\text{Al}_2\text{S}_2$  core is folded slightly (fold angle 167.5°) along the S(1)⋯S(2) axis. Although each Al is complexed by one  $\text{Me}_2\text{SO}$ , it can be seen from Fig. 2 that the relative orientation of each donor molecule is different. Thus, the  $\text{Me}_2\text{SO}$  containing O(1) is oriented such that the  $\text{SMe}_2$  moiety lies above the  $\text{Al}_2\text{S}_2$  core whereas the O(2) containing  $\text{Me}_2\text{SO}$  is oriented away from the core. These different orientations are reflected in different Al–O–S angles of 114.2(2)° at O(1) and 130.0(2)° at O(2). It seems that this unusual arrangement is a result of some weak intermolecular interactions involving the  $\text{Me}_2\text{SO}$  donor containing O(2). These interactions involve relatively short O⋯H distances [*e.g.* O(2)⋯H(40E) 2.89 Å, O(2)⋯H(39F) 2.63 Å], and S⋯H distances [*e.g.* S(1)⋯H(39C) 3.04 Å, S(2)⋯H(40E) 3.02 Å]. Another notable feature of the structure of **2** is the distorted geometry at the *ipso*-C atoms of the  $\text{Mes}^*$  ligands. The averaged aromatic ring planes are bent by *ca.* 25° from the Al–C vector lines. Similar distortions have been observed in other  $\text{Mes}^*$  group 13 derivatives.<sup>10</sup>

Finally, although no dissociation of the dimeric **1** was effected by the addition of  $\text{Me}_2\text{SO}$ , attempted redissolution of isolated **2** results in its partial decomposition and production of



**Fig. 2** Computer generated drawing of **2**. H atoms, except those involved in intermolecular interactions, are not shown. Some important bond distances (Å) and angles (°): Al(1)–S(1) 2.259(2), Al(1)–S(2) 2.243(2), Al(2)–S(1) 2.258(2), Al(2)–S(2) 2.247(2), Al(1)–O(1) 1.869(2), Al(2)–O(2) 1.847(3), Al(1)–C(1) 2.014(4), Al(2)–C(21) 2.029(4), S(3)–O(1) 1.553(3), S(4)–O(2) 1.548(3), Al(1)···Al(2) = 2.999(2), S–C(Me) av 1.766(8); S(1)–Al(1)–S(2) 95.91(6), S(1)–Al(2)–S(2) 95.84(6), Al(1)–S(1)–Al(2) 83.20(5), Al(1)–S(2)–Al(2) 83.83(5), S(1)–Al(1)–C(1) 118.79(12), S(2)–Al(1)–C(1) 118.25(12), O(1)–Al(1)–C(1) 115.30(14), O(2)–Al(2)–C(21) 115.16(14), S(3)–O(1)–Al(1) 114.2(2), S(4)–O(2)–Al(2) 130.0(2).

an orange–red solid. Attempts to identify the composition of this solid are currently underway.

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## Notes and References

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† Alumoxanes of formula  $R_2AlOAlR_2$  can be synthesized by the reaction of triorganoaluminium compounds with species containing reactive oxygen such as  $CO_2$ ,  $RC(O)NR_2$ ,  $MeCO_2H$  and  $Me_2SO$ . See: H. Sinn and W. Kaminsky, *Adv. Organomet. Chem.*, 1980, **18**, 99; W. Uhl, M. Koch, W. Hiller and M. Heckel, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 989.

‡ The compound  $S(SiMe_3)_2$  has been extensively used recently in the synthesis of several transition metal sulfide cluster compounds. See: D. Fenske and S. Dehnen, *Chem. Eur. J.*, 1996, **2**, 1407.

§ All manipulations were carried out under anaerobic and anhydrous conditions. The compound  $(Mes^*AlH_2)_2^5$  was synthesized as described in the literature and  $S(SiMe_3)_2$  was purchased from Aldrich and used as received.

**1** or **1-PhMe**: A solution of  $(Mes^*AlH_2)_2^5$  (1.05 g, 1.91 mmol) in toluene (25 ml) was heated with  $(Me_3Si)_2S$  (0.81 ml, 3.82 mmol, 0.68 g) at room temp. The clear, colorless solution was heated to 100–105 °C for ca. 21 h during which time large colorless plates of **1-PhMe** formed. Yield: 1.25 g, 93%. Mp: turns opaque at 120–140 °C (desolvation), melts at 305–310 °C. Crystals of unsolvated **1** suitable for X-ray diffraction studies were obtained via a similar procedure by the reaction of  $(Mes^*AlH_2)_2$  with  $(Me_3Si)_2S$  in *n*-octane at 115–120 °C for 38 h. Yield: 42%. Mp: turns slowly opaque at 250–280 °C, melts at 310–312 °C.  $^1H$  NMR ( $C_6D_6$ , 85 °C):  $\delta$  7.51 (s, *m*-H, 4 H), 1.81 (s, *o*-CH<sub>3</sub>, 36 H), 1.36 (s, *p*-CH<sub>3</sub>, 18 H).

**2**: Dimethyl sulfoxide (0.06 ml, 0.8 mmol, 0.062 g) was added to a slurry of finely ground **1-PhMe** (0.16 g, 0.23 mmol) in benzene (25 ml) at room temp. to give an almost clear solution from which after a few seconds a fine, colorless solid precipitates. This was dissolved by heating to reflux for ca. 1 min to afford a clear colorless solution from which, after 3 days at room temp. ca. 0.04 g of colorless plates could be isolated. Yield: 23%. Mp: turns red at 235 °C, gradually darkens to almost black at 300 °C, does not melt below 300 °C.

It is noteworthy that **1** is practically insoluble in hydrocarbon solvents. It can be solubilized by the addition of  $Me_2SO$  or HMPA at elevated temperatures (the range 60–80 °C works best). From these solutions crystals are usually obtained upon cooling to room temp. These crystals do not redissolve without decomposition.

¶ Crystal data at  $T = 130$  K with Mo-K $\alpha$ , ( $\lambda = 0.71073$  Å) radiation for **1** and Cu-K $\alpha$ , ( $\lambda = 1.54178$  Å) radiation for **2**: **1**,  $C_{36}H_{58}Al_2S_2$ ,  $M = 608.9$ , monoclinic, space group  $C2/c$ ,  $a = 26.924(5)$ ,  $b = 9.845(2)$ ,  $c = 16.780(3)$  Å,  $\beta = 125.86(3)^\circ$ ,  $U = 3064(1)$  Å<sup>3</sup>,  $\mu = 0.219$  mm<sup>-1</sup>,  $Z = 4$  (8/2),  $wR_2 = 0.119$  for all 4149 data,  $R_1 = 0.047$  for 3164 [ $I > 2\sigma(I)$ ] data; **2**,  $C_{40}H_{70}Al_2O_2S_4$ ,  $M = 765.2$  monoclinic, space group  $P2_1/n$ ,  $a = 18.374(5)$ ,  $b = 9.883(2)$ ,  $c = 24.587(3)$  Å,  $\beta = 91.16(2)^\circ$ ,  $U = 4464(2)$  Å<sup>3</sup>,  $\mu = 2.560$  mm<sup>-1</sup>,  $Z = 4$ ,  $wR_2 = 0.143$  for all 5830 data,  $R_1 = 0.053$  for 4550 [ $I > 2\sigma(I)$ ] data. CCDC 182/706.

- 1 A. R. Barron, *Comments Inorg. Chem.*, 1993, **14**, 123.
- 2 (a) A. H. Cowley, R. A. Jones, P. R. Harris, D. A. Atwood, L. Contreras and C. J. Burek, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1143; (b) M. B. Power and A. R. Barron, *J. Chem. Soc., Chem. Commun.*, 1991, 1315; (c) M. B. Power, J. W. Ziller, A. N. Tyler and A. R. Barron, *Organometallics*, 1992, **11**, 1055; (d) C. J. Harlan, E. G. Gillan, S. G. Bott and A. R. Barron, *Organometallics*, 1996, **15**, 5479; (e) S. L. Stoll, S. G. Bott and A. R. Barron, *J. Chem. Soc., Dalton Trans.*, 1997, 1315.
- 3 M. K. Mason, J. M. Smith, S. G. Bott and A. R. Barron, *J. Am. Chem. Soc.*, 1993, **115**, 4971.
- 4 R. J. Wehmschulte and P. P. Power, *J. Am. Chem. Soc.*, 1997, **119**, 8387.
- 5 R. J. Wehmschulte and P. P. Power, *Inorg. Chem.*, 1994, **33**, 5611.
- 6 K. Ruhlandt-Senge and P. P. Power, *Inorg. Chem.*, 1991, **30**, 2633.
- 7 W. Uhl, A. Vester and W. Miller, *J. Organomet. Chem.*, 1993, **443**, 9.
- 8 A. Boardman, R. W. H. Small and I. J. Worrall, *Inorg. Chim. Acta*, 1986, **120**, L23.
- 9 M. B. Power, S. G. Bott, D. L. Clark, J. L. Atwood and A. R. Barron, *Organometallics*, 1990, **9**, 3086.
- 10 A. Meller, S. Pusch, E. Pohl, L. Häming and R. Herbst-Irmer, *Chem. Ber.*, 1993, **126**, 2255; H. Rahbarnoochi, M. Heeg and J. P. Oliver, *Organometallics*, 1994, **13**, 2123; (c) R. J. Wehmschulte, J. J. Ellison, K. Ruhlandt-Senge and P. P. Power, *Inorg. Chem.*, 1994, **33**, 6300.

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