DALTON

Alane– and gallane–sulfur donor chemistry: synthesis of $AlH_3 \cdot NMe(CH_2CH_2)_2S$, $\{AlH_2[\mu\text{-}N(CH_2CH_2)_2S]\}_2$ and $MH(SCH_2CH_2NEt_2)_2$ (M = Al or Ga)

Cameron Jones,[a] **Fu Chin Lee,**[a] **George A. Koutsantonis,**[a] **Michael G. Gardiner**[b] **and Colin L. Raston** *,[b]

[a] *Faculty of Science and Technology, Griffith University, Nathan, Brisbane, Queensland, 4111, Australia*

[b] *Department of Chemistry, Monash University, Clayton, Victoria, 3168, Australia*

Reaction of *N*-methylthiomorpholine hydroiodide with $LiAlH_4$ in OEt_2 yielded the Lewis-base adduct of alane, $AlH_3 \cdot NMe(CH_2CH_2)_2S$ **1**, which is monomeric in benzene as the N-donor species. Thiomorpholine with $H_3Al \cdot NMe_3$ also in OEt_2 afforded the metallated species $\{AlH_2[\mu\text{-}N(CH_2CH_2)_2S]\}_2$ **2**; in the solid-state dimers arising from bridging amido centres are weakly associated *via* intermolecular Al ··· S interactions at 3.22(3) Å. Treatment of 2-diethylaminoethanethiol hydrochloride with $LiMH_4$ (M = Al or Ga) in OEt_2 or tetrahydrofuran generated the five-co-ordinate species $MH(SCH_2CH_2NEt_2)_2$ (M = Al **3** or Ga **4**), authenticated by X-ray crystallography as isostructural, chiral five-co-ordinate species in the solid, the N-donor groups occupying apical positions of trigonal-bipyramidal metal centres.

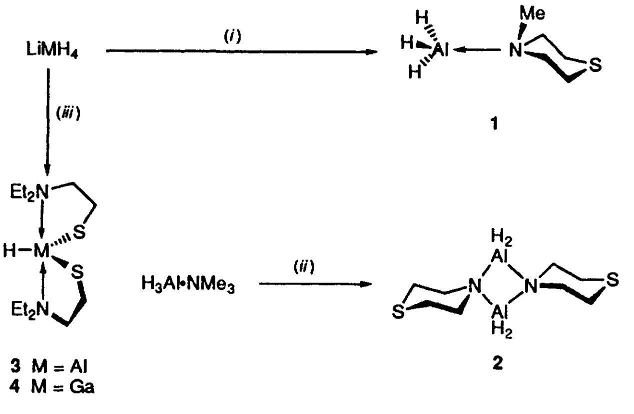
As an extension of a systematic study of the chemistry of alane, AlH_3, and gallane, GaH_3,[1–6] primarily as Lewis-base adducts, we have investigated the complexation of sulfur-donor complexes as well as some thiolate derivatives. There have been few studies of sulfur-donor complexation of alane,[7] and there is none for gallane. Indeed, there are only a few well characterised Group 16 donor adducts/complexes of the metal hydrides, notably tetrahydrofuran (thf) adducts of alane,[8] but not gallane, and alkoxide species.[9] This is in contrast to a wide variety of Lewis-base adducts alone, including tertiary amines and phosphines, for both alane and gallane,[1,10] which are useful reagents for metallation,[4,6,7,11] reduction of unsaturated compounds,[4,5,12] and applications in chemical vapour deposition (CVD) technology.[1,13] In the context of CVD-generated metal sulfides, thin films of gallium sulfide have been grown from alkylmetal sulfide and thiolate clusters.[14]

The limited thiolate alane chemistry includes metallation of propanethiol using $H_3Al \cdot NMe_3$ which is thought to proceed through an unstable five-co-ordinate alane intermediate, $H_3Al \cdot NMe_3 \cdot PrSH$.[7] This is consistent with the tendency for alane (but not gallane) to form hypervalent five-co-ordinate species.[1] The product is partially associated, *via* thiolato or hydrido bridges. With respect to the latter it is noteworthy that this type of association for tertiary amine adducts of alane is inherently weak, the association energy being within the realms of crystal-packing forces.[15] S-Donor interactions for aluminium in general are weak,[16] and in the case of thiophene–dimethylaluminium species there is a reluctance to form any intimate metal–sulfur contact, even at the expense of electron-deficient C-centred bridging at the 2 position of the thiophene.[17] Thiolates bridging aluminium, and also gallium, through the S prevail unless steric factors intervene.[18]

Herein we report (*i*) the synthesis of the *N*-methylthiomorpholine adduct of alane **1**, (*ii*) the synthesis and structural elucidation of the N-bridging dimeric amido species **2**, derived from metallation of thiomorpholine using $H_3Al \cdot NMe_3$, the compound being weakly associated in the solid *via* Al ··· S interactions, and (*iii*) the synthesis (*via* metallation) and structure determinations of the chiral, five-co-ordinate thiolato species $MH(SCH_2CH_2NEt_2)_2$, (M = Al **3** or Ga **4**).

Results and Discussion

The reactions are summarised in Scheme 1. While compound **1** has minimum association in benzene (association degree 1.06, Signer method[19]), any association in the solid *via* Al ··· S interactions is likely to be weak. Unfortunately suitable crystals for X-ray diffraction studies could not be obtained. The O-donor analogue of **1** is polymeric in the solid,[20] with the O of one molecule bound to the metal centre of another molecule, the O and N atoms being in apical positions of trigonal-bipyramidal metal centres. The O ··· Al contact appears to be weak, having a bond length greater than that normally seen for Al–O dative bonds. Thus the primary co-ordination is from the N-donor functionality with a weaker secondary co-ordination from the O-donor of another molecule. This is consistent with theoretical studies on the model compound $H_3Al \cdot NH_3 \cdot H_2O$.[3] Any S–Al dative bond in **1** should be weaker than the Al–O bond in the corresponding oxygen analogue, assuming adherence to the basicity series (N > O > S) established for donor complexes of aluminium Lewis acids. The solution ^{27}Al NMR chemical shift of compound **1**, δ 140.6, is similar to that of the oxygen-centred analogue, δ 142.2, and is consistent with



Scheme 1 (*i*) *N*-Methylthiomorpholine hydroiodide; $-H_2$, $-LiI$, M = Al; (*ii*) thiomorpholine, $-H_2$; (*iii*) $Et_2N(CH_2)_2SH \cdot HCl$, $-LiCl$, $-H_2$

J. Chem. Soc., Dalton Trans., 1996, Pages 829–833

four-fold co-ordination of the metal centres of both compounds in solution.

Five-fold co-ordination for tertiary amine adducts of alane is usually achieved by complexation of additional amine, *e.g.* $H_3Al{\cdot}2NMe_3$, or other Lewis bases. This includes the formation of other mixed-donor adducts, $(Me_3N{\cdot}AlH_3)_2{\cdot}(PMe_2CH_2)_2$[20] and $Me_3N{\cdot}AlH_3{\cdot}PBu^t{}_3$.[21] The stabilisation energy of phosphine adducts relative to free phosphine and amine adducts of alane is only a few kcal mol^{-1}.[20] Five-fold co-ordination for tertiary amine adducts is also achieved *via* hydride bridging.[15] Even so, four-co-ordination is possible in the solid, notably $AlH_3{\cdot}L$ (L = quinuclidine,[20] $PBu^n{}_3$[21] or (2,2,6,6-tetramethylpiperidine[6]).

Compound **2** was characterised by NMR spectroscopy and a crystal structure determination which established the primary structure to be based on a dimeric amide-bridged species with four-membered Al_2N_2 rings. The compound crystallises in the orthorhombic space group *Ibam* with four centrosymmetric dimers in the unit cell, each residing on a crystallographic mirror and C_2 axis, Fig. 1 and 2. The Al_2N_2 ring is a common structural motif for a wide range of aluminium amido species, including the hydrido species $[(AlH_2)_2(\mu\text{-}NBu^tCH_2)_2]$,[6] $[(H_2Al)(NPr^i{}_2)]_2$[22] and $[HAl(\mu\text{-}NMe_2)(NMe_2)]_2$.[23] (Steric hindrance at the N-amido centre can result in bridging through the hydrido groups rather than the amido groups, $\{H(\mu\text{-}H)Al[N(CHMeCH_2)_2CH_2]\}_3$ and $\{(\mu\text{-}H)Al[N(CMe_2CH_2)_2CH_2]_2\}_2$.[24]) However, in the case of **2** the dimeric structure is weakly associated in the solid as a two-dimensional polymeric network *via* intermolecular Al···S interactions, Fig. 2. In contrast, it is thought that the morpholine analogue of **2**, $\{AlH_2[N(CH_2CH_2)_2O]\}_\infty$, exists as a linear polymer *via* intermolecular oxygen donation.[25] Attempts to prepare the gallium analogue of **2**, and also **1**, resulted in decomposition yielding gallium metal.

The location of the hydrido groups establishes the geometry of the aluminium centres as being distorted four-co-ordinate, although there are weak Al···S intermolecular interactions at 3.22(3) Å which is less than the van der Waals radii for the two atoms (3.9 Å);[26] the interaction is opposite a bridging nitrogen centre, S···Al–N 174.3(2)°. The Al–N distances, 1.962(6) and 1.996(6) Å, are within the realms of those normally seen for oligomeric alane amido species, *e.g.* 1.966(2) Å in $[HAl(\mu\text{-}NMe_2)(NMe_2)]_2$.[23]

Compounds **3** and **4** were prepared by treatment of the hydrochloride salt of 2-diethylaminoethanethiol with 1 equivalent of $LiMH_4$ in diethyl ether, Scheme 1. The aluminium compound was also prepared, albeit in low yield, by treating 2-diethylaminoethanethiol hydrochloride with $K[HBBu^s{}_3]$ then $H_3Al{\cdot}NMe_3$ in thf. Here the $K[HBBu^s{}_3]$ was effective as an unconventional base for generating the free thiol, $HSCH_2CH_2NEt_2$. Treatment of $H_3Al{\cdot}NMe_3$ with an equimolar amount of the same thiol, however, afforded an intractable brown oil. The formation of the bis(thiolate) compounds even using 1 equivalent of the hydrochloride is noteworthy; the use of 2 equivalents also gives **3** or **4**, although in diminished yields. Any monothiolato species, $MH_2(SCH_2CH_2NEt_2)$, generated during the reaction may undergo redistribution to solvated **3** or **4** and solvated MH_3 although, given the instability of GaH_3 with respect to formation of gallium and hydrogen, 'ate' species with LiCl are more likely, for example $Li^+MClH_3{}^-$. The formation of monohydrido species is different to the formation of compound **2**, where 1 equivalent of hydrohalide affords a stable dihydrido species, presumably due to the more strongly bridging amido centres.

Attempts were made to model the extended Al···S interaction in compound **2** using theoretical calculations (GAUSSIAN 92)[27] but all calculations diverged giving the hydride-bridged dimer.

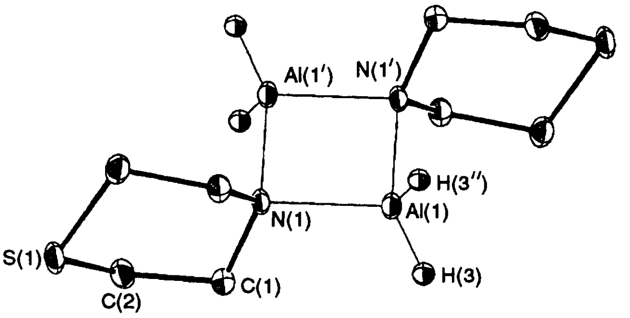


Fig. 1 Projection of $\{AlH_2[\mu\text{-}N(CH_2CH_2)_2S]\}_2$ **2**, showing 20% probability ellipsoids. Selected bond distances (Å) and angles (°): Al(1)–N(1) 1.962(6), Al(1)–N(1') 1.996(6), Al(1)–H(3) 1.37(2), Al···Al' 2.821(5); N(1)–Al(1)–N(1') 89.1(3), N(1)–Al(1)–H(3) 110(1), H(1)–Al–N' 105(1), H(3)–Al–H(3'') 128(3) and Al(1)–N(1)–Al(1') 90.9(3)

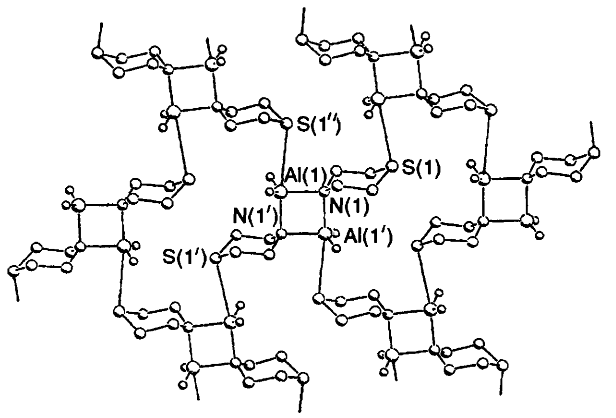


Fig. 2 Portion of the unit cell showing extended intermolecular contacts. Al(1)···S'' 3.22(3) Å, N(1)–Al(1)···S'' 85.07(9) and N(1')–Al(1)···S'' 174.3(2)°

Proton NMR data are consistent with compounds **3** and **4** being fluxional in solution. The methylene groups of the chelate rings show complex multiplets in the range δ 2.1–2.7 which is consistent with the presence of chelating rings. The ^{13}C NMR spectra have only a single resonance for each of the methylene and methyl groups, suggesting a fluxional molecule, based on the five-co-ordinate structure in the solid. The fluxional process in solution involving rapid interchange of ligands possibly proceeds *via* four-co-ordinate species with one nitrogen remote from the metal centre. Four-co-ordination is preferred for gallane species, but not alane species where five- and even six-co-ordination is possible.[1]

Suitable crystals of compounds **3** and **4** for structure determinations were grown from thf and diethyl ether respectively. They are isostructural, crystallising in the space group $P2_12_12_1$ with one molecule in the asymmetric unit, Fig. 3. The metal centres are trigonal bipyramidal with the overall molecular symmetry approximating to C_2, the symmetry axis coinciding with the H–M vector; the hydrido group, metal centre and the two S atoms constitute the trigonal plane [Σ(S–M–S,H) angles = 360.0, 356.3° respectively] with the nitrogen centres in apical positions. The structure determination of the gallium compound is of low precision and the hydride was poorly defined, whereas the aluminium compound revealed a well resolved hydride with associated geometry typical of terminal Al–H species.[15]

The M–N distances are significantly different, mean 2.18, 2.27 respectively, which is consistent with the differences in electronegativity of the two metals. The Al–N distances are similar to those in bis(tertiary amine) adducts of alane which also have the N-donors in apical positions of trigonal-bipyramidal structures, *e.g.* $\{AlH_3[NMe_2(CH_2)_3NMe_2]\}_\infty$, 2.200(4) and 2.217(4) Å.[28] There are no comparable distances for gallane, bis(tertiary amines) being intrinsically unstable.[1] The

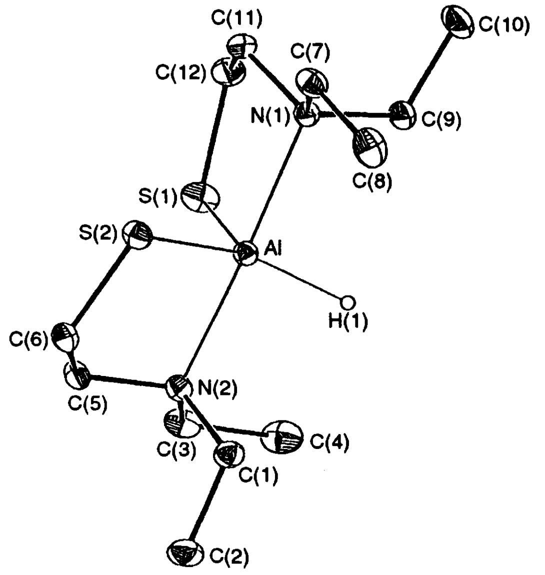


Fig. 3 Molecular projection of $\mathrm{AlH(SCH_2CH_2NEt_2)_2}$, **3**, showing 20% probability ellipsoids for the non-hydrogen atoms and arbitrary radii for the hydrides. Selected bond distances (Å) and angles (°) (corresponding values for the isostructural gallium analogue **4**, in square brackets. Al–S(1) 2.271(1) [2.288(3)], Al–S(2) 2.278(1) [2.289(2)], Al–N(1) 2.175(2) [2.252(9)], Al–N(2) 2.182(2) [2.28(1)], and Al–H(1) 1.62(2) [1.33]; S(1)–Al–S(2) 116.41(4) [115.3(1)], S(1)–Al–N(1) 86.33(6) [85.9(2)], S(1)–Al–N(2) 93.04(7) [92.7(2)], S(1)–Al–H(1) 123.6(8) [123.0], S(2)–Al–N(1) 92.27(6) [92.7(2)], S(2)–Al–N(2) 86.50(7) [85.5(2)], S(2)–Al–H(1) 120.0(8) [118.2], N(1)–Al–N(2) 178.2(1) [177.1(3)], N(1)–Al–H(1) 90.9(8) [73.6] and N(2)–Al–H(1) 90.9(8) [109.3]

Al–S distances, mean 2.275 Å, are significantly shorter than Al–S distances in other thiolate structures where bridging sulfur centres are prevalent, *e.g.* 2.405(8) Å in $\mathrm{[AlMe_2(\mu\text{-}SC_6F_5)]_2}$,[29] but as expected are longer than those in monomeric, three-co-ordinate thiolate species, *viz.* 2.185(8) Å in $\mathrm{Al(SC_6H_2Bu^t{}_3\text{-}2,4,6)_3}$.[18] Similarly the Ga–S distances are shorter than Ga–S distances for doubly bridging systems (2.36–2.40 Å),[18] and also longer than in monomeric, three-co-ordinate species, 2.205(1) Å in $\mathrm{Ga(SC_6H_2Bu^t{}_3\text{-}2,4,6)_3}$.[18]

Conclusion

Well characterised sulfur-donor adducts of alane and gallane remain elusive. Replacing a hydrido by an S-donor-functionalised amido group results in some weak Al • • • S interaction for alane, at least in the solid state, the corresponding gallium compound being inaccessible. Using anionic sulfur-centred ligands, however, results in stable metal-sulfur linkages and the potential bridging of the sulfur-centres is blocked by pendant N-donor groups.

Experimental

General

All manipulations were carried out using standard Schlenk and glove-box techniques under an atmosphere of high-purity argon or nitrogen. Solvents were dried then freeze/thaw-degassed prior to use. Thiomorpholine and 2-ethylaminoethanethiol hydrochloride were obtained from Aldrich, the former being distilled over sodium wire at reduced pressure. *N*-Methylthiomorpholine hydroiodide was prepared according to the literature procedure.[30] Proton NMR spectra were recorded on Bruker WM-250 and CXP-300 and Varian Gemini-200 and Unity-400 spectrometers in deuteriated benzene or toluene and referenced to the residual ^{1}H resonances of the solvent (δ 7.15 and 6.98, respectively), ^{13}C NMR spectra in deuteriated benzene or thf on the same spectrometers using broad-band proton decoupling and referenced to the ^{13}C resonances of the deuteriated solvent (δ 128.00) and ^{27}Al NMR spectra on a Bruker CXP-300 spectrometer in deuteriated benzene or toluene and referenced to external $\mathrm{[Al(H_2O)_6]^{3+}}$ (1 mol dm^{-3} in water). Elemental analyses were performed by the Canadian Microanalytical Services Ltd., Vancouver, and the Chemical and Micro Analytical Services Pty. Ltd., Melbourne. Melting points were determined in sealed glass capillaries under argon, and are uncorrected.

Syntheses

$\mathrm{AlH_3{\cdot}NMe(CH_2CH_2)_2S}$ 1. *N*-methylthiomorpholine hydroiodide (1.18 g, 4.8 mmol) was added to a solution of $\mathrm{LiAlH_4}$ (0.18 g, 4.7 mmol) in $\mathrm{OEt_2}$ (40 cm^3) at −80 °C. After gas evolution had ceased the resulting suspension was warmed to room temperature and filtered. The filtrate was reduced to *ca.* 20 cm^3 under vacuum and placed at −20 °C affording colourless prisms (0.59 g, 85% yield), m.p. 72–73 °C. NMR ($\mathrm{C_6D_6}$): ^{1}H (250 MHz), δ 1.86 (3 H, s, NMe), 2.17 (4 H, m, $\mathrm{NCH_2}$), 2.56 (4 H, t, $^3J_{\mathrm{HH}} = 5$ Hz, $\mathrm{CH_2S}$) and 3.82 (3 H, br s, AlH); ^{13}C (62.8 MHz), δ 23.6 ($\mathrm{SCH_2}$), 43.1 (NMe) and 54.8 ($\mathrm{NCH_2}$); ^{27}Al (78.2 MHz), δ 140.6, $w_{\frac{1}{2}}$ 1900 Hz. IR 1750 (br) cm^{-1} [ν(Al–H)]. *M* 156 ± 15 (degree of association 1.06 ± 0.10) (Found: C, 40.05; H, 8.95; N, 9.25. Calc. for $\mathrm{C_5H_{14}AlNS}$: C, 40.80; H, 9.60; N, 9.50%).

$\mathrm{\{AlH_2[\mu\text{-}N(CH_2CH_2)_2S]\}_2}$ 2. Thiomorpholine (0.54 cm^3, 0.56 g, 5.4 mmol) was added to a solution of $\mathrm{H_3Al{\cdot}NMe_3}$ (0.48 g, 5.4 mmol) in $\mathrm{OEt_2}$ (40 cm^3) at −80 °C. Upon warming to room temperature gas was evolved and a white solid deposited which was isolated, dried *in vacuo* and sublimed (0.2 mmHg, *ca.* 26.6 Pa) at 150 °C yielding large colourless prisms (0.49 g, 69% yield), m.p. 214–216 °C (decomp. 240 °C). NMR: ^{1}H (250 MHz, $\mathrm{C_6D_6}$), δ 2.25 (4 H, m, $\mathrm{SCH_2}$), 2.77 (4 H, m, $\mathrm{NCH_2}$) and 4.15 (2 H, br s, AlH); ^{13}C (62.8 MHz, [^{2}H$_8$]thf), δ 29.1 ($\mathrm{SCH_2}$) and 49.1 ($\mathrm{NCH_2}$) IR 1825 (br) cm^{-1} [ν(Al–H)] (Found: C, 35.55; H, 7.10; N, 10.70. Calc. for $\mathrm{C_4H_{10}AlNS}$: C, 36.60; H, 7.70; N, 10.70%).

$\mathrm{AlH(SCH_2CH_2NEt_2)_2}$ 3. Solid 2-diethylaminoethanethiol hydrochloride (1.16 g, 6.83 mmol) was added to a thf solution (30 cm^3) of $\mathrm{LiAlH_4}$ (0.26 g, 6.85 mmol) at 0 °C. After gas evolution had ceased the resulting mixture was brought to room temperature and stirred for 3 h, then filtered and the filtrate concentrated (*ca.* 10 cm^3) and stored overnight at −30 °C affording colourless cubic crystals (0.68 g, 68%), m.p. 136–138 °C; NMR ($\mathrm{C_6D_6}$): ^{1}H (200 MHz), δ 0.91 (12 H, t, $^3J_{\mathrm{HH}} =$ 7.2, $\mathrm{CH_3}$), 2.84 (8 H, q, $^3J_{\mathrm{HH}} = 7.2$ Hz, $\mathrm{NCH_2}$), 2.1–2.7 (8 H, m, $\mathrm{SCH_2CH_2}$), and 4.5 (1 H, br, AlH); ^{13}C (50.3 MHz), δ 9.98 ($\mathrm{SCH_2}$), 22.6, 24.1 ($\mathrm{CH_3}$), 45.4 ($\mathrm{N\mathit{C}H_2CH_2}$), 53.7, 55.1 ($\mathrm{N\mathit{C}H_2CH_3}$); ^{27}Al (52.11 MHz), δ 109.9, $w_{\frac{1}{2}}$ 1980 Hz, IR 1790(br) cm^{-1} [ν(Al–H)] (Found: C, 47.90; H, 9.40; N, 9.35; S, 21.70. Calc. for $\mathrm{C_{12}H_{29}AlN_2S_2}$: C, 49.30; H, 10.00; N, 9.60; S, 21.90%).

$\mathrm{GaH(SCH_2CH_2NEt_2)_2}$ 4. Solid 2-diethylaminoethanethiol hydrochloride (1.40 g, 8.27 mmol) was added to a diethyl ether solution (30 cm^3) of $\mathrm{LiGaH_4}$ (10 cm^3, 8.27 mmol) at 0 °C. After gas evolution had ceased the resulting mixture was brought to room temperature and stirred for 3 h, then filtered and the filtrate concentrated (*ca.* 8 cm^3) and stored overnight at −30 °C affording colourless cubic crystals (0.98 g, 71%), m.p. 96–98 °C. NMR ($\mathrm{C_6D_6}$): ^{1}H (200 MHz), δ 0.77 (12 H, t, $^3J_{\mathrm{HH}} = 7.2$ Hz, $\mathrm{CH_3}$), 2.1–2.7 (16 H, m, $\mathrm{CH_2CH_2NCH_2}$), and 5.34 (1 H, br, GaH); ^{13}C (50.3 MHz), δ 8.1 ($\mathrm{SCH_2}$), 24.9 ($\mathrm{CH_3}$), 43.0 ($\mathrm{N\mathit{C}H_2CH_3}$), and 53.9 ($\mathrm{N\mathit{C}H_2CH_2}$). IR 186 (br) cm^{-1} [ν(Ga–H)] (Found: C, 39.70; H, 7.60; N, 7.45. Calc. for $\mathrm{C_{12}H_{29}GaN_2S_2}$: C, 43.00; H, 8.70; N, 8.35%).

Table 1 Crystal data for $\{AlH_2[\mu\text{-}N(CH_2CH_2)_2S]\}_2$ **2** and $MH(SCH_2CH_2NEt_2)_2$ (M = Al **3** or Ga **4**) at 23 °C, λ = 0.710 73 Å

	2	**3**	**4**
Formula	$C_8H_{20}Al_2N_2S_2$	$C_{12}H_{29}AlN_2S_2$	$C_{12}H_{29}GaN_2S_2$
M	234.33	292.48	335.21
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Ibam* (no. 72)	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)
a/Å	12.343(3)	9.642(2)	9.704(3)
b/Å	9.092(2)	12.487(3)	12.428(2)
c/Å	11.623(3)	13.734(2)	13.656(2)
U/Å^3	1304.4(8)	1653.5(5)	1646.8(6)
Z	8	4	4
D_c/g cm^{-3}	1.336	1.175	1.352
Crystal dimensions/mm	0.4 × 0.3 × 0.3	0.4 × 0.4 × 0.4	0.3 × 0.3 × 0.3
μ(Mo-Kα)/cm^{-1} (no correction)	5.11	3.53	1.91
F(000)	560	640	712
No. unique reflections	1041	1675	1177
No. reflections with $I > 2.5\sigma(I)$	536	1517	1114
$2\theta_{max}$/°	60	50	50
R	0.066	0.024	0.043
R'	0.075	0.025	0.049

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$.

Table 2 Non-hydrogen atom and hydride positional parameters for $\{AlH_2[\mu\text{-}N(CH_2CH_2)_2S]\}_2$ **2**

Atom	X/a	Y/b	Z/c
S(1)	0.6565(2)	0.4485(2)	0.50
Al(1)	0.5854(2)	−0.1031(3)	0.50
N(1)	0.5762(5)	0.1123(6)	0.50
C(1)	0.6249(5)	0.1770(6)	0.6053(6)
C(2)	0.6026(5)	0.3428(7)	0.6185(6)
H(3)	0.617(3)	−0.153(5)	0.6063

Table 3 Non-hydrogen atom and hydride positional parameters for $AlH(SCH_2CH_2NEt_2)_2$ **3**

Atom	X/a	Y/b	Z/c
Al	0.977 13(8)	0.501 22(6)	0.482 81(5)
S(1)	0.063 04(8)	0.562 88(7)	0.626 23(5)
S(2)	1.026 44(8)	0.600 33(6)	0.347 95(5)
N(1)	0.793 5(2)	0.596 0(2)	0.515 0(2)
N(2)	1.165 0(2)	0.410 8(2)	0.449 8(2)
C(1)	1.121 9(3)	0.326 0(2)	0.378 6(2)
C(2)	1.237 2(4)	0.261 8(3)	0.331 0(2)
C(3)	1.238 5(3)	0.362 7(3)	0.534 9(2)
C(4)	1.155 9(4)	0.283 7(3)	0.593 7(2)
C(5)	1.260 8(3)	0.489 5(3)	0.403 9(2)
C(6)	1.195 9(3)	0.545 6(3)	0.318 0(2)
C(7)	0.713 2(3)	0.634 3(2)	0.428 3(2)
C(8)	0.658 1(3)	0.545 6(3)	0.364 0(3)
C(9)	0.705 0(3)	0.528 7(2)	0.580 5(2)
C(10)	0.575 0(3)	0.581 0(3)	0.621 9(3)
C(11)	0.846 4(3)	0.692 9(2)	0.566 5(2)
C(12)	0.932 7(3)	0.664 1(2)	0.654 5(2)
H(1)	0.884(2)	0.394(2)	0.473(2)

Table 4 Non-hydrogen atom and hydride positional parameters, for $GaH(SCH_2CH_2NEt_2)_2$ **4**

Atom	X/a	Y/b	Z/c
Ga	0.976 8(1)	0.498 86(9)	0.483 92(6)
S(1)	1.063 6(4)	0.562 4(2)	0.628 5(2)
S(2)	1.029 5(4)	0.599 3(2)	0.348 5(2)
N(1)	0.789(1)	0.598 8(6)	0.518 0(5)
N(2)	1.173(1)	0.405 3(6)	0.449 0(5)
C(1)	1.131(1)	0.319 1(7)	0.379 3(7)
C(2)	1.244(2)	0.255 8(8)	0.329 8(8)
C(3)	1.253(1)	0.361 2(8)	0.534 1(7)
C(4)	1.164(2)	0.281 3(9)	0.595 7(7)
C(5)	1.266(1)	0.485 7(9)	0.400 1(7)
C(6)	1.190(1)	0.542 1(8)	0.316 1(7)
C(7)	0.711(1)	0.638 2(8)	0.430 5(7)
C(8)	0.657(2)	0.549(1)	0.366 1(8)
C(9)	0.696(1)	0.531 4(7)	0.583 1(7)
C(10)	0.573(1)	0.582 1(9)	0.623 8(8)
C(11)	0.845(1)	0.693 7(8)	0.571 3(7)
C(12)	0.932(1)	0.662 3(8)	0.657 6(7)
H(1)	0.869 0	0.432 6	0.479 1

Structure determinations

Crystals suitable for structure determination were grown by sublimation (**2**) or crystallisation from OEt_2 (**3**) or thf (**4**) at −30 °C and were mounted in sealed capillaries under an argon atmosphere. Unique diffractometer data sets were measured using Enraf-Nonius CAD4 diffractometers. Reflections with $I > 2.5\sigma(I)$ were considered 'observed' and used in the full-matrix least-squares refinements, minimizing $\Sigma w\Delta^2$ after solution of the structures by direct methods with σ weighting applied. Conventional residuals on F at convergence are quoted. No extensive, significant extinction effects were found. Neutral-atom complex scattering factors were employed.[31] Computation used the XTAL 3.0[32] and TEXSAN[33] program systems. Crystal data and atom coordinates are given in Table 1–4. Anisotropic thermal parameters were refined for all non-hydrogen atoms in the three structure determinations. Hydrogen atoms attached to carbon and the hydrido groups were located and refined for compound **2**, and included as invariants (C–H 0.95 Å) for **3**, hydride excepted which was refined in (x,y,z,U), and **4**. Thermal parameters for methyl hydrogen atoms were estimated at approximately 1.5 U_{ii}(average) of the attached carbon atom and 1.25 U_{ii}(average) for other hydrogen atoms. The alternative optical isomers for **3** and **4** made no significant difference to the R values.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Acknowledgements

Finances provided by the Australian Research Council and the Department of Industry, Technology and Commerce (Australia) in support of this work are gratefully acknowledged, and we thank Colin Kennard and Karl Byriel for collecting some of the X-ray diffraction data.

References

1 M. R. Mason and A. R. Barron, *Chemtracts, Inorg. Chem.*, 1992, **4**, 179; C. Jones, G. A. Koutsantonis and C. L. Raston, *Polyhedron*, 1993, **12**, 1829; C. L. Raston, *J. Organomet. Chem.*, 1994, **475**, 15 and refs. therein.

2 G. A. Koutsantonis, Fu Chin Lee and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1994, 1975.

3 F. M. Elms, R. N. Lamb, P. J. Pigram, M. G. Gardiner, B. J. Wood and C. L. Raston, *Chem. Mater.*, 1994, **6**, 1059.

4 J. L. Atwood, Fu Chin Lee, C. L. Raston and K. D. Robinson, *J. Chem. Soc., Dalton Trans.*, 1994, 2019.

5 C. Tranter, A. F. Siu, C. L. Raston and D. J. Young, *Tetrahedron Lett.*, 1994, **35**, 5915.

6 J. L. Atwood, S. M. Lawrence and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1994, 73; J. L. Atwood, G. A. Koutsantonis, Fu-Chin Lee and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1994, 91.

7 W. Marconi, A. Mazzei, F. Bonati and M. de Malde, *Z. Naturforsch., Teil B*, 1963, **18**, 3.

8 I. B. Gorrell, P. B. Hitchcock and J. D. Smith, *J. Chem. Soc., Chem. Commun.*, 1993, 189.

9 M. D. Healy, M. R. Mason, P. W. Gravelle, S. G. Bott and A. R. Barron, *J. Chem. Soc., Dalton Trans.*, 1993, 441 and refs. therein; S. J. Rettig, A. Storr and J. Trotter, *Can. J. Chem.*, 1975, **53**, 58; G. A. Koutsantonis, Fu Chin Lee and C. L. Raston, *Main Group Chem. J.*, 1995, **1**, 21.

10 D. O'Hare, J. S. Foord, T. C. Page and T. J. Whitaker, *J. Chem. Soc., Chem. Commun.*, 1991, 1445 and refs. therein.

11 J. L. Atwood, S. G. Bott, C. Jones and C. L. Raston, *Inorg. Chem.*, 1991, **30**, 4868; *J. Chem. Soc., Chem. Commun.*, 1992, 1349.

12 M. J. Henderson, C. H. L. Kennard, C. L. Raston and G. Smith, *J. Chem. Soc., Chem. Commun.*, 1990, 1203; E. M. Marlett and W. S. Park, *J. Org. Chem.*, 1990, **55**, 2968 and refs therein.

13 D. M. Frigo, G. J. M. van Eijden, P. J. Reuvers and C. J. Smit, *Chem. Mater.*, 1994, **6**, 190 and refs. therein.

14 A. MacInnes, M. B. Power and A. R. Barron, *Chem. Mater.*, 1993, **5**, 1344.

15 J. L. Atwood, F. R. Bennett, F. M. Elms, C. Jones, C. L. Raston and K. D. Robinson, *J. Am. Chem. Soc.*, 1991, **113**, 8183.

16 H. Rahbarnoohi, R. Kumar, M. J. Heeg and J. P. Oliver, *Organometallics*, 1994, **13**, 3300.

17 D. G. Hendershot, M. Barber, R. Kumar and J. P. Oliver, *Organometallics*, 1992, **10**, 3302.

18 K. Ruhlandt-Senge and P. P. Power, *Inorg. Chem.*, 1991, **30**, 2633 and refs. therein.

19 B. J. Burger and J. E. Bercaw, in *Experimental Organometallic Chemistry*, eds. A. L. Wayda and M. Y. Darensbourg, American Chemical Society, New York, 1987, ch. 4.

20 K. W. Butz, M. G. Gardiner, C. Jones, G. A. Koutsantonis and C. L. Raston, *Inorg. Chem.*, 1993, **32**, 3482.

21 F. M. Elms, M. G. Gardiner, G. A. Koutsantonis, C. L. Raston, J. L. Atwood and K. D. Robinson, *J. Organomet. Chem.*, 1993, **449**, 45.

22 G. Perego, G. Del Piero, M. Corbellini and M. Bruzzone, *J. Organomet. Chem.*, 1977, **136**, 301.

23 K. Ouzounis, H. Riffel, H. Hess, U. Kohler and J. Weidlein, *Z. Anorg. Allg. Chem.*, 1983, **504**, 67.

24 C. Kein, H. Nöth, M. Tacke and M. Thomann, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 886.

25 W. Marconi, A. Mazzei, F. Bonati and M. de Malde, *Gazz. Chim. Ital.*, 1962, **92**, 1062.

26 J. Emsley, *The Elements*, Clarendon, Oxford, 1989.

27 GAUSSIAN 92/DFT, Revision G.4; cG.4, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. W. Wong, J. B. Foresman, M. A. Robb, M. Head-Gordon, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1993.

28 J. L. Atwood, F. R. Bennett, C. Jones, G. A. Koutsantonis, C. L. Raston and K. D. Robinson, *J. Chem. Soc., Chem. Commun.*, 1992, 541.

29 V. S. De Mel, R. Kumar and J. P. Oliver, *Organometallics*, 1990, **9**, 1303.

30 D. J. Burinsky and J. E. Campana, *Org. Mass. Spectrom.*, 1984, **19**, 539.

31 *International Tables for X-Ray Crystallography*, eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4.

32 *XTAL User's Manual—Version 3.0*, eds. S. R. Hall and J. M. Stewart, The Universities of Western Australia and Maryland, 1990.

33 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985 and 1992.

Received 7th August 1995; *Paper* 5/05261K