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Oligomeric structures of the crystalline dimethylamine adducts $Me_2(H)N{\cdot}MH_3$ (M = Al or Ga) and the dimethylamido derivative $[Me_2NGaH_2]_3$

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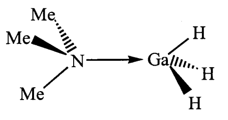
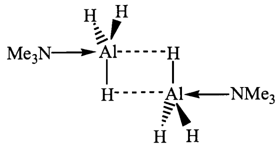
The adduct $Me_2(H)N{\cdot}AlH_3$ (**1**) has been isolated for the first time at low temperatures from the reaction of $[Me_2NH_2]Cl$ with $LiAlH_4$ in Et_2O solution at *ca.* 250 K. Single crystals of this and of the corresponding gallane $Me_2(H)N{\cdot}GaH_3$ (**2**) have been grown, also at low temperature; the structures of these at 150 K determined by X-ray diffraction reveal dimeric units $Me_2(H)N{\cdot}H_2M(\mu\text{-}H)_2MH_2{\cdot}N(H)Me_2$ with highly unsymmetrical M–H $\cdots$ M hydrogen bridges, as well as evidence of significant *inter*molecular N–H $\cdots$ H–M interactions, particularly for M = Al. The M–N distances are quite similar [**1** 2.028(1), **2** 2.079(3) Å], but the M $\cdots$ M distance in **2** [3.7519(15) Å] is much longer than in **1** [2.8743(8) Å]. The adducts decompose at ambient temperatures, rapidly in the case of **1**, slowly in the case of **2**, with the elimination of H_2 and the formation of the corresponding dimethylamido derivative. Unlike the vapour at low pressure in which the dimeric molecule predominates, crystals of the gallane (**3**) at 150 K are composed of trimers $[Me_2NGaH_2]_3$ structurally analogous to the corresponding alane, with a chair-like conformation and a mean Ga–N distance of 1.981(3) Å.

Significantly weaker Lewis acids than the corresponding trihalides, alane and gallane are known nevertheless to form numerous adducts with neutral bases or anionic species.[1–5] Complexation is a key factor in the stabilisation of the parent hydride; in the case of aluminium, this is perhaps less important than the increased tractability of the adducts. For reasons of thermal stability, solubility in common organic solvents, or ease of preparation and manipulation, therefore, species like $Me_3N{\cdot}MH_3$ (M = Al or Ga) make altogether more convenient synthetic agents than do the base-free hydrides in reactions seeking to exploit the facility of the metal-bound hydrogen ligands to act as leaving groups in metathesis, reduction or elimination. Accordingly, the adducts have found significant applications not only in chemical synthesis,[3–5] but also in chemical vapour deposition (CVD) technology.[2–8] In addition to the synthesis and characterisation of new complexes of the Group 13 metal hydrides, there have been numerous quantum chemical studies assessing the structural, vibrational and thermodynamic properties of species like $H_3E{\cdot}MH_3$ (M = Al or Ga; E = N[9–11] or P[9,12]) and $H_2O{\cdot}MH_3$ (M = Al or Ga).[13]

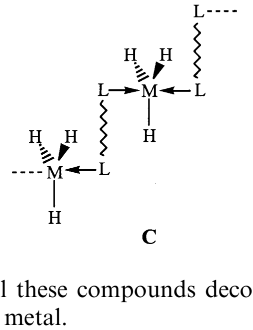
Tertiary amines form more or less stable adducts with alane and gallane with quite a diverse range of structural types.[3–5] Whereas $Me_3N{\cdot}GaH_3$ consists of discrete molecules (**A**) in the vapour and solid phases,[14] for example, the corresponding alane is monomeric in the vapour[15] but dimeric in the crystalline phase.[16] The structure in the last case, which is also favoured by some other unidentate amine[16,17] and ether[18] adducts of alane, consists of a central Al_2H_6 unit held together by highly unsymmetrical hydrogen bridges (**B**). The tendency of aluminium to take up five-fold coordination is also revealed by the oligomeric complexes which alane forms with polydentate tertiary amines (as in **C**),[19] with yet another variant being provided by the formation of ionic species, *e.g.* $[H_2AlL]^+[AlH_4]^-$ where L = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine.[20] With but few exceptions, all these compounds decompose thermally to give the Group 13 metal.



A



B



C

By contrast, secondary amines are usually metallated in the presence of alane or gallane, with the elimination of dihydrogen and the formation of the corresponding amidometal derivative (eqn. (1)), with a facility that increases in the order B < Ga < Al.[1]

$$R_2(H)N{\cdot}MH_3 \longrightarrow \frac{1}{n}[R_2NMH_2]_n + H_2 \qquad (1)$$

For example, the dimethylamine adduct $Me_2(H)N{\cdot}GaH_3$ has been isolated as a liquid which loses dihydrogen slowly at ambient temperatures,[1,21,22] whereas the corresponding alane has not been isolated hitherto, having been reported to decompose rapidly at temperatures in excess of 263 K.[23] Only with the appropriately bulky secondary amine 2,2,6,6-tetramethylpiperidine has it been possible to prepare a thermally stable adduct of alane;[24] the crystalline solid contains monomeric

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molecules with a structure similar to **A** except that the ligands assume an *eclipsed* conformation about the Al–N bond. Amido derivatives of alane and gallane, as formed in eqn. (1), are typically dimers or trimers based on 4-membered or 6-membered MN cyclic cores, respectively, according to the bulk of the ligands R linked to nitrogen.[4–6] In this respect, dimethylamidoalane appears to differ from the corresponding gallane: crystals of the aluminium compound are composed of trimeric units each containing a 6-membered $[AlN]_3$ ring,[25] yet the predominant species in the vapour of the gallane is the dimer with a 4-membered $[GaN]_2$ skeleton.[22]

Here we report the isolation of the dimethylamine adduct of alane, $Me_2(H)N{\cdot}AlH_3$ **1**, by crystallisation from diethyl ether solution at *ca.* 203 K. Structural characterisation at 150 K shows a dimeric structure similar to that of $Me_3N{\cdot}AlH_3$.[16] Controlled cooling of the liquid gallane adduct, $Me_2(H)N{\cdot}GaH_3$, **2**, initially at 242 K has also allowed crystals to be grown. Here too X-ray structural analysis elicits a dimeric structure, with the first sighting of what might be described as an adduct of digallane. However, the M–H···M bridges are even more unsymmetrical and the metal···metal distance considerably longer than are the corresponding units in the alane. Decomposition of the gallane gives dimethylamidogallane, **3**, crystals of which at 150 K have been shown to be isomorphous with those of the corresponding alane,[25] being composed not of dimeric but of trimeric molecules, $[Me_2NGaH_2]_3$. The studies also give evidence of unconventional 'dihydrogen' bonds, $N\text{–}H^{\delta+}\cdots{}^{\delta-}H\text{–}M$,[26] of the sort disclosed by the structures of the crystalline compounds $H_3B{\cdot}NH_3$[27] and $[H_2GaNH_2]_3$,[28] and which may play a major role in directing not just the course of decomposition, but also the topology of the decomposition product, *e.g.* GaN.[28]

Experimental

Synthesis

Dimethylamine–alane, $Me_2(H)N{\cdot}AlH_3$ **1**, was prepared by the reaction of $LiAlH_4$ with $[Me_2NH_2]Cl$ (both ex Aldrich Chemicals and freshly recrystallised) in dry Et_2O solution at *ca.* 248 K. After filtering the cold solution, crystallisation of the adduct was brought about by cooling to 203 K. The crystals were stable *in vacuo* at temperatures up to *ca.* 250 K, but decomposed rapidly at ambient temperatures with the release of H_2 and the formation of white, needle-like crystals of dimethylamidoalane, $[Me_2NAlH_2]_3$.[25]

$LiGaH_4$ was prepared by the reaction of LiH with $GaCl_3$ (both ex Aldrich Chemicals) in Et_2O[29] and the reaction of a sample freshly recrystallised from Et_2O with $[Me_2NH_2]Cl$, again in Et_2O solution, afforded dimethylamine–gallane, $Me_2(H)N{\cdot}GaH_3$ **2**.[21,22] A liquid at room temperature, this was purified by fractional condensation *in vacuo*, the purity being checked by reference to the IR spectrum of the solid condensate formed at 77 K and to the ^1H NMR spectrum of a $[^2H_8]$toluene solution. A sample was then loaded *in vacuo* into a pre-conditioned[30] Pyrex capillary of 0.4 mm external diameter for the purpose of crystal growth. Once a column of liquid 1.5–2 cm in depth had collected, the sample was cooled to 77 K and the capillary sealed to give a total length not exceeding 3 cm.

A portion of dimethylamine–gallane was left *in vacuo* at room temperature for about 14 days to bring about the formation of white needle-like crystals of dimethylamidogallane, **3**, in accordance with eqn. (1).[22] The amido derivative was in turn purified by vacuum sublimation and authenticated by its IR and ^1H NMR spectrum.[21,22]

Growth and/or manipulation of crystals for X-ray diffraction

Single crystals of dimethylamine–gallane, **2**, were grown by careful cooling, with the capillary containing the initially liquid sample mounted on the diffractometer. The capillary was fixed to a goniometric head and mounted in the cold stream of an Oxford Cryosystems low-temperature device attached to a Stoë Stadi four-circle diffractometer.[31] A stable solid–liquid phase boundary was established within the sample at 241.7 K, and crystallisation induced by cooling at approximately 20 K h^{-1}; a data set was collected with the crystal at 150 K. The crystal so formed proved to be a twin (see below); a second crystal was grown under similar conditions except that the cooling ramp rate was set at 1 K h^{-1}. Data were collected with the crystal at 230 K, but ramping to 150 K caused the diffraction quality to deteriorate and so no data were collected at this temperature. The results from the second crystal are similar to those obtained from the first at 150 K except that the Ga–H bond lengths appeared to be librationally shortened to 1.40(3) Å and several contact distances were longer, for example Ga···Ga 3.8289(9) Å, H···Ga 3.02(3) Å, NH···HGa 2.27 and 2.42 Å. We prefer to discuss in detail the data derived from the twinned structure since they were collected at the same temperature as those for **1** and **3**. However, data derived from the untwinned crystal have also been deposited.

Crystals of dimethylamine–alane, **1**, grown at 203 K from diethyl ether solution, were collected at low temperature and handled under cold RS3000 perfluoropolyether oil. A crystal of dimethylamidogallane, **3**, was grown by zone-refinement of a sample held in a capillary over a period of 14 h using a SciConsult OHCD laser-assisted crystal-growing device. Crystallographic data were collected on a Bruker Smart Apex CCD diffractometer, again equipped with an Oxford Cryostream operating at 150 K.

All data sets were collected with Mo-Kα radiation.

Crystallography: data collection, structure solution and refinement

Details of the data and data collection for crystals of the compounds **1**, **2** and **3** are given in Table 1.

(*a*) Dimethylamine–alane, 1, and dimethylamidogallane, 3. Absorption corrections were performed using the programme SADABS,[32] and the crystal structures solved by direct methods (SHELXS[33]). Hydrogen atoms attached to carbon were placed in calculated positions whereas those attached to aluminium, gallium or nitrogen were located in difference maps and refined freely. All non-hydrogen atoms were modelled with anisotropic displacement parameters. Both refinements proceeded by full-matrix least squares against F^2 (SHELXL).[34]

(*b*) Dimethylamine–gallane, 2. The diffraction pattern of a crystalline sample could be indexed (DIRAX)[35] on the basis of a large monoclinic *I*-centred unit cell with dimensions $a = 10.39$, $b = 6.37$, $c = 49.73$ Å; $\beta = 90.5°$. The true cell, which has one-third the volume of this cell, was recognised by noting that reflections collected on this unit cell tended to be weak unless $h + 2l = 3n$.

An absorption correction was performed by Gaussian integration following optimisation of the morphology and dimensions of a general cylindrical crystal against a set of ψ-scans (Stoe X-Shape). The structure was solved by Patterson methods (DIRDIF)[36] and could be developed by least-squares refinement and difference syntheses (SHELXL).[34] This refinement converged to a rather high $R1$ of 7%, while a difference map calculated at this stage contained peaks of between 1 and 2 e $Å^{-3}$ in chemically implausible positions.

The monoclinic *I*-centred supercell is approximately orthorhombic, and it seemed reasonable that this crystal structure was twinned, a two-fold rotation about the *a*-axis of the cell being taken as the twin law. With respect to the axes of the true cell, the rotation is given by the matrix $(-1\ 0\ -0.695/0\ -1\ 0/0\ 0\ 1)$. The off-diagonal term herein is fairly close to 2/3 (but not

Table 1 Crystal data, data collection and structure refinement for dimethylamine–alane, **1**, dimethylamine–gallane, **2**, and dimethylamidogallane, **3**

	1	**2**	**3**
Empirical formula	$C_4H_{20}Al_2N_2$	$C_2H_{10}GaN$	$C_2H_{24}Ga_3N_3$
Formula weight	150.18	117.83	347.44
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/c$
a/Å	8.5594(19)	16.965(5)	6.4821(11)
b/Å	6.0337(13)	6.365(2)	8.7304(14)
c/Å	11.022(2)	10.395(3)	25.350(4)
β/°	105.967(3)	102.29(2)	92.795(3)
Volume/Å^3	547.3(2)	1096.7(6)	1432.9(4)
Z	2	8	4
Density (calc.)/Mg m^{-3}	0.911	1.427	1.611
Absorption coefficient/mm^{-1}	0.203	4.850	5.567
Reflections collected	2993	5929	9051
Independent reflections	1121 (R_{int} 0.0186)	976 (R_{int} 0.0566)	3569 (R_{int} 0.0536)
Conventional R [$F > 4\sigma(F)$]	R_1 0.0257 (987 data)	R_1 0.0365 (760 data)	R_1 0.0334 (2353 data)
Weighted R (F^2 and all data)	0.0786	0.0953	0.0646

Table 2 Selected bond distances (Å) and angles (°) for crystalline dimethylamine–alane, **1**, at 150 K[a]

Al(1)–N(1)	2.0281(11)	Al(1)#1–Al(1)–H(2X)	99.9(4)
Al(1)···Al(1)#1	2.8743(8)	H(1X)–Al(1)–H(2X)	122.5(6)
Al(1)–H(1X)	1.549(13)	N(1)–Al(1)–H(3X)	94.0(5)
Al(1)–H(2X)	1.545(11)	Al(1)#1–Al(1)–H(3X)	44.4(5)
Al(1)–H(3X)	1.543(12)	H(1X)–Al(1)–H(3X)	119.7(7)
N(1)–C(2)	1.4703(16)	H(2X)–Al(1)–H(3X)	114.4(6)
N(1)–C(1)	1.4714(16)	C(2)–N(1)–C(1)	110.87(10)
N(1)–H(1N)	0.824(14)	C(2)–N(1)–Al(1)	112.97(8)
Al(1)#1···H(3X)	2.075(16)	C(1)–N(1)–Al(1)	113.88(8)
N(1)–Al(1)–Al(1)#1	138.30(4)	C(2)–N(1)–H(1N)	110.2(9)
N(1)–Al(1)–H(1X)	97.5(5)	C(1)–N(1)–H(1N)	107.3(9)
Al(1)#1–Al(1)–H(1X)	104.9(5)	Al(1)–N(1)–H(1N)	101.0(9)
N(1)–Al(1)–H(2X)	96.9(4)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + 1$, $-y$, $-z$. For the methyl groups, the C–H bond distances were fixed at 0.98 Å and the H–C–H angles at 109.5°.

exactly so because β in the supercell deviates slightly from 90°), and splitting the intensities of reflections with $l = 0$ and 3 over both components was found to be a satisfactory model for the twinning. Splitting other reflections, such as layers with $l = 6$, 9, *etc.* and $l = 10$ led to no improvement.

The H atom attached to N(1) was placed in a calculated position and allowed to ride on its parent atom. Other H atoms were located in difference syntheses, those attached to carbon being treated as rotating rigid groups, while those attached to Ga were refined with the Ga–H distances restrained to be equal and a common isotropic displacement parameter. Non-H atoms were modelled with anisotropic displacement parameters. The refinement converged to a conventional $R1$ of 3.65% and a twin scale factor of 0.206(6).

CCDC reference numbers 162421–162424 (this includes the data relating to the untwinned crystal of $Me_2(H)N·GaH_3$ at 240 K).

See http://www.rsc.org/suppdata/dt/b1/b102667b/ for crystallographic data in CIF or other electronic format.

Results and discussion

Crystal structure of dimethylamine–alane at 150 K

The structure of $Me_2(H)N·AlH_3$ at 150 K is illustrated in Fig. 1. Salient bond distances and angles are listed in Table 2. The results show that the solid consists of dimeric units $Me_2(H)N·H_2Al(\mu\text{-}H)_2AlH_2·N(H)Me_2$. The structural motif is thus analogous to that found in the crystalline complexes formed by alane with 1 mol each of the tertiary amine Me_3N,[16] $Me_2(PhCH_2)N$,[16] $Me_2(ClCH_2CH_2CH_2)N$,[17] and *N*-methyl-2,5,6-trihydropyridine[16] or the ether tetrahydrofuran.[18] As in those cases, **1** can be viewed as a 1 : 2 adduct of the elusive dialane, Al_2H_6, with the two metal atoms linked *via* two distinctly unsymmetrical Al–H···Al bridges, the two arms of the bridge measuring 1.543(12) and 2.075(16) Å, respectively. The sum of the three H–Al–H angles is very close to 360° (357° in fact), so that each aluminium centre enjoys what approximates to trigonal bipyramidal coordination with two apical linkages comprising (i) the bond to the amine ligand and (ii) the longer of the two Al–H bridge bonds. That the two $Me_2(H)N·AlH_3$ fragments are bound together only weakly in the dimeric unit is evident not only in the length of these bridge bonds, but also in the finding that the shorter Al–H bridge bonds are no longer than the terminal Al–H ones. At 2.8743(8) Å, the separation between the two Al atoms in the dimer is well within the range reported (2.862–2.900 Å) on the basis (i) of earlier crystallographic studies of tertiary amine complexes having analogous structures[16,17] and (ii) of *ab initio* molecular orbital calculations on the model system $[H_3N·AlH_3]_2$.[16] That the Al–N distances are 0.04–0.06 Å shorter in **1** than in the tertiary amine complexes[16,17] is consistent with the superior basicity (deriving at

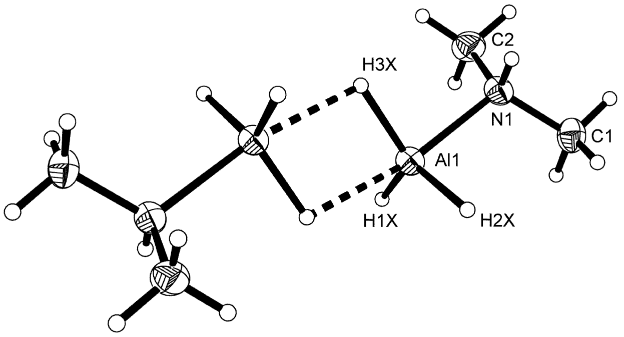

Fig. 1 Structure of solid $Me_2(H)N·AlH_3$ at 150 K as determined by X-ray diffraction.

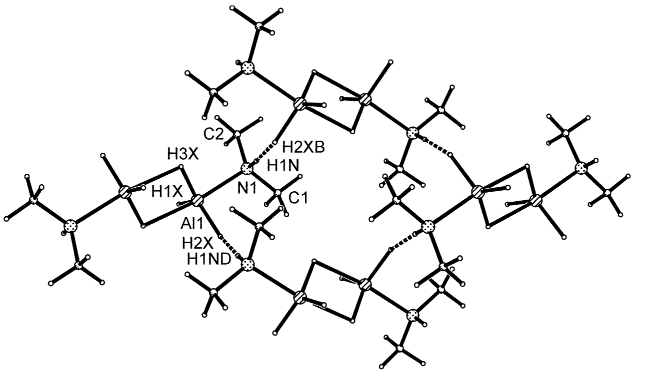

Fig. 2 Structure of solid $Me_2(H)N\cdot AlH_3$ at 150 K illustrating the intermolecular N–H · · · H–Al contacts.

least in part from the greater dipole moment[37]) of the secondary amine Me_2NH. The distances are not significantly different from the not particularly well defined one [2.04(1) Å] in monomeric $Me_2\overline{CCH_2CH_2CH_2CMe_2N}H\cdot AlH_3$.[24]

The dimeric units apart, the structure is also notable for revealing significant *inter*molecular N–H · · · H–Al contacts of 1.925(19) Å involving Al–H(2)X (see Fig. 2). The $[Me_2(H)N\cdot AlH_3]_2$ molecules form a two-dimensional network in which the repeat unit is a ring containing four molecules. The H · · · H distance is well within the range 1.7–2.2 Å and the interaction is also marked by a near linear N–H · · · H and bent H · · · H–Al unit [N–H · · · H = 175.9(15)°, H · · · H–Al = 139.2(9)°], all features deemed to be characteristic of 'dihydrogen' bonds.[26,27] The interactions are presumed to influence the torsional angles about the Al–N bond, although the arrangement of the substituents about this bond is staggered and not eclipsed, as in the case of $Me_2\overline{CCH_2CH_2CH_2CMe_2N}H\cdot AlH_3$.[24] The H · · · H distance we find in crystalline **1** is actually somewhat shorter than those determined, admittedly by neutron diffraction, in solid $H_3N\cdot BH_3$ [2.02(3) Å for the shortest H · · · H distance between *monomeric* $H_3N\cdot BH_3$ molecules][27] or $[H_2GaNH_2]_3$ {1.97(2) Å for the shortest H · · · H distance between the cyclic, chairlike $[H_2GaNH_2]_3$ molecules}.[28] Calculations have suggested[27,28] that each H · · · H dihydrogen bond contributes between 12 and 32 kJ mol^{-1} to the binding energy in the gallium and boron compounds, respectively. The Al–H bond is appreciably more polar than either the B–H or the Ga–H bond, and so stronger H · · · H bonds are to be expected in solid dimethylamine–alane.

Earlier quantum chemical calculations[11] predicted head-to-tail aggregation of $H_3N\cdot AlH_3$ to form a dimer in which the two fragments are twisted relative to each other so as to form two H · · · H bonds each involving one N–H and one Al–H unit. This results not only in a more or less eclipsed conformation of the substituents about each of the Al–N bonds but also in H · · · H separations estimated to fall in the range 1.78–2.00 Å. In the event, solid **1** shows a staggered conformation for the $Me_2(H)N\cdot AlH_3$ unit; the shortest *intra*molecular H · · · H distances within the dimer measure 2.37 Å and are not therefore significantly different from twice the contact radius of hydrogen (2.40 Å).[38] Hence it is not within but *between* the dimers that H · · · H interaction appears to be a significant influence and may well prefigure a step along the reaction coordinate leading to the decomposition of the adduct with the formation of H_2 and cyclic dimethylamidoalane, $[Me_2NAlH_2]_3$.[25] In a similar way, the crystal structure of cyclotrigallazane, $[H_2GaNH_2]_3$, which also features intermolecular H · · · H bonding, appears to foreshadow the decomposition of this compound to GaN not in the normal wurtzite but in a cubic (zinc blende) modification.[28]

Crystal structure of dimethylamine–gallane at 150 K

Under similar conditions, crystalline dimethylamine–gallane, **2**, shows a superficial resemblance to the alane. As represented in Fig. 3, the solid is again made up of dimeric units $Me_2(H)N\cdot H_2Ga(\mu\text{-}H)_2GaH_2\cdot N(H)Me_2$; relevant dimensions are listed in Table 3.

Table 3 Selected bond distances (Å) and angles (°) for crystalline dimethylamine–gallane, **2**, at 150 K[a]

Ga(1)–N(1)	2.079(3)	H(1)–Ga(1)–H(2)	111(3)
Ga(1)–H(1)	1.50(3)	N(1)–Ga(1)–H(3)	102.3(19)
Ga(1)–H(2)	1.49(3)	H(1)–Ga(1)–H(3)	111(3)
Ga(1)–H(3)	1.50(3)	H(2)–Ga(1)–H(3)	126(3)
N(1)–C(1)	1.475(6)	C(1)–N(1)–C(2)	111.5(3)
N(1)–C(2)	1.477(6)	C(1)–N(1)–Ga(1)	111.1(3)
N(1)–H(1N)	0.93	C(2)–N(1)–Ga(1)	111.6(3)
Ga(1) · · · Ga(2)	3.7519(15)	C(1)–N(1)–H(1N)	107.4
Ga(2) · · · H(3)	2.87(5)	C(2)–N(1)–H(1N)	107.4
N(1)–Ga(1)–H(1)	102(2)	Ga(1)–N(1)–H(1N)	107.4
N(1)–Ga(1)–H(2)	101(2)		

[a] For the methyl groups, the C–H bond distances were fixed at 0.97 Å and the H–C–H angles at 109.5°.

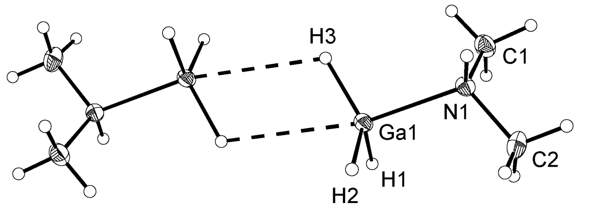

Fig. 3 Structure of solid $Me_2(H)N\cdot GaH_3$ at 150 K as determined by X-ray diffraction.

This is the first example of a solid gallane complex that can be formally regarded as a 1 : 2 adduct of digallane, Ga_2H_6,[39] or as a stage in the cleavage of the Ga–H–Ga bridges of this molecule *en route* to the simple 1 : 1 adduct $Me_2(H)N\cdot GaH_3$ which appears to be the sole component of the vapour at pressures in the order of 1 Torr (133 Pa).[40] By contrast, there is no hint of a similar dimeric unit in the crystal structure of the trimethylamine adduct $Me_3N\cdot GaH_3$ at 150 K.[14] To what extent this difference depends on the smaller size of Me_2NH compared with Me_3N and/or on the superior basicity of the secondary amine it is impossible to judge on the evidence at present available. On the other hand, the central $Ga(\mu\text{-}H)_2Ga$ bridge is even more unsymmetrical than in the alane complex, the two arms of each bridge measuring 1.50(3) and 2.87(5) Å. Accordingly the Ga · · · Ga separation is, at 3.7519(15) Å, considerably greater than the Al · · · Al separation in the alane complex. Aluminium and gallium differ but little in covalent or contact radii and so the difference inevitably reflects the weakness of the Ga–H · · · Ga secondary bonding in the dimer, together with the general reluctance of gallium to assume a coordination number greater than four.[1,4–6] As in the alane, there is no measurable difference in the length of the three Ga–H bonds [1.50(3) Å] in each $Me_2(H)N\cdot GaH_3$ fragment, irrespective of which may be involved in bridging to a second such fragment. The weakness of the interaction between the fragments is also signalled by the angular geometry of the GaH_3 unit, which, unlike the AlH_3 unit in the alane complex, takes the form of a shallow pyramid, with the H–Ga–H angles summing to 348°. Indeed, with a mean semi-vertical angle of 78° the GaH_3 pyramid appears to be slightly less flattened in the crystalline dimethylamine adduct than in the corresponding (monomeric) trimethylamine derivative (where the angle is 83°).[14] This, allied to the staggered conformation of the $Me_2(H)N\cdot GaH_3$ units, suggests that the geometry of the GaH_3 groups is determined more by the enhanced basicity of the secondary amine than by the requirements of dimerisation. On the other hand, the Ga–N distance is only marginally shorter in the dimethylamine complex [2.079(3) *vs.* 2.081(4) Å[14]], and in this respect the move towards five-fold coordination of the gallium centres may go

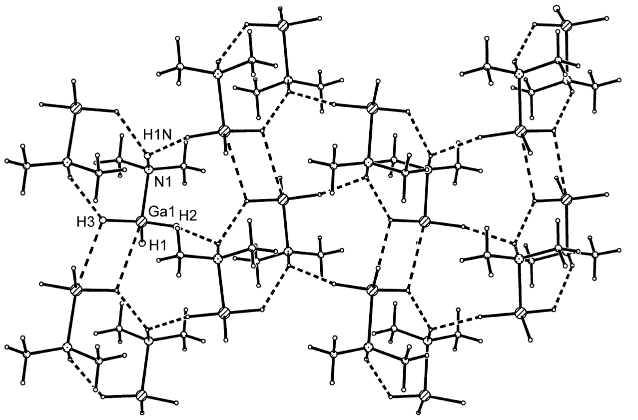

Fig. 4 One of the layers that form the structure of solid $Me_2(H)N·GaH_3$ at 150 K.

some way towards counteracting the effect of base strength. That base strength does have a significant influence is more clearly revealed by comparison with other gallane adducts that have been characterised crystallographically. Thus, the Ga–N distances in $HC(CH_2CH_2)_3N·GaH_3$,[41] $Me_2(PhCH_2)N·GaH_3$,[17] and $H_3Ga·Me_2NCH_2CH_2NMe_2·GaH_3$,[42] all of which contain only tetra-coordinated gallium centres, are 2.063(4), 2.071(3) and 2.094(4) Å, respectively. The sole gallane complex featuring an unequivocally penta-coordinated metal atom and for which the crystal structure has been determined is that formed by *N*,*N*,*N*′,*N*′-tetramethylpropylenediamine; this has a polymeric structure of the type **C** and features much longer Ga–N distances averaging 2.36 Å.[42]

As in the case of **1**, the molecules of **2** are packed so as to form a layered structure; Fig. 4 affords a view of one such layer. Again there are N–H···H–M contacts between the $Me_2(H)N·GaH_3$ molecules of different dimeric units. At 2.23(8) [to H(3)] and 2.32(6) Å [to H(2)], however, these are appreciably longer than in the case of the alane adduct. Hence they fall outside the range prescribed for significant dihydrogen bonding,[26,27] being not far short of the limit of 2.40 Å set by twice the contact radius of hydrogen.[38] Moreover, there is a distinct change in the form of the intermolecular contacts, with each N–H bond interlocking not with a single Ga–H bond but with two such bonds in a bifurcated array of the sort familiar enough with conventional hydrogen bonding.[43] The much reduced H···H interaction in the gallane complex is understandable in terms of the reduced basicity of hydrogen atoms bound to gallium, as opposed to aluminium; with the barest hint of H_2 preformation, it is also wholly consistent with the comparative reluctance of the complex to decompose in accordance with eqn. (1).

Table 4 Selected bond distances (Å) and angles (°) for crystalline dimethylamidogallane, **3**, at 150 K[a]

Ga(1)–N(1)	1.980(3)	N(1)–Ga(2)–H(22)	107.8(10)
Ga(1)–N(3)	1.984(3)	N(2)–Ga(2)–H(22)	105.6(10)
Ga(1)–H(11)	1.510(17)	H(21)–Ga(2)–H(22)	122.7(15)
Ga(1)–H(12)	1.522(16)	N(3)–Ga(3)–N(2)	108.21(11)
Ga(2)–N(1)	1.979(3)	N(3)–Ga(3)–H(31)	106.1(11)
Ga(2)–N(2)	1.991(3)	N(2)–Ga(3)–H(31)	109.5(11)
Ga(2)–H(21)	1.499(17)	N(3)–Ga(3)–H(32)	106.8(11)
Ga(2)–H(22)	1.520(16)	N(2)–Ga(3)–H(32)	107.0(11)
Ga(3)–N(3)	1.971(3)	H(31)–Ga(3)–H(32)	118.8(15)
Ga(3)–N(2)	1.982(3)	C(12)–N(1)–C(11)	106.8(3)
Ga(3)–H(31)	1.505(16)	C(12)–N(1)–Ga(2)	112.4(2)
Ga(3)–H(32)	1.515(17)	C(11)–N(1)–Ga(2)	105.3(2)
N(1)–C(12)	1.489(4)	C(12)–N(1)–Ga(1)	112.1(2)
N(1)–C(11)	1.491(4)	C(11)–N(1)–Ga(1)	105.4(2)
N(2)–C(22)	1.480(4)	Ga(2)–N(1)–Ga(1)	114.06(12)
N(2)–C(21)	1.482(4)	C(22)–N(2)–C(21)	106.9(3)
N(3)–C(32)	1.489(4)	C(22)–N(2)–Ga(3)	113.2(2)
N(3)–C(31)	1.493(4)	C(21)–N(2)–Ga(3)	105.0(2)
N(1)–Ga(1)–N(3)	107.74(11)	C(22)–N(2)–Ga(2)	113.0(2)
N(1)–Ga(1)–H(11)	108.1(12)	C(21)–N(2)–Ga(2)	104.1(2)
N(3)–Ga(1)–H(11)	108.7(11)	Ga(3)–N(2)–Ga(2)	113.66(13)
N(1)–Ga(1)–H(12)	106.4(10)	C(32)–N(3)–C(31)	106.0(3)
N(3)–Ga(1)–H(12)	108.6(10)	C(32)–N(3)–Ga(3)	104.8(2)
H(11)–Ga(1)–H(12)	116.9(15)	C(31)–N(3)–Ga(3)	112.4(2)
N(1)–Ga(2)–N(2)	108.65(11)	C(32)–N(3)–Ga(1)	104.8(2)
N(1)–Ga(2)–H(21)	106.8(11)	C(31)–N(3)–Ga(1)	112.4(2)
N(2)–Ga(2)–H(21)	104.7(11)	Ga(3)–N(3)–Ga(1)	115.29(13)

[a] For the methyl groups, the C–H bond distances were fixed at 0.98 Å and the H–C–H angles at 109.5°.

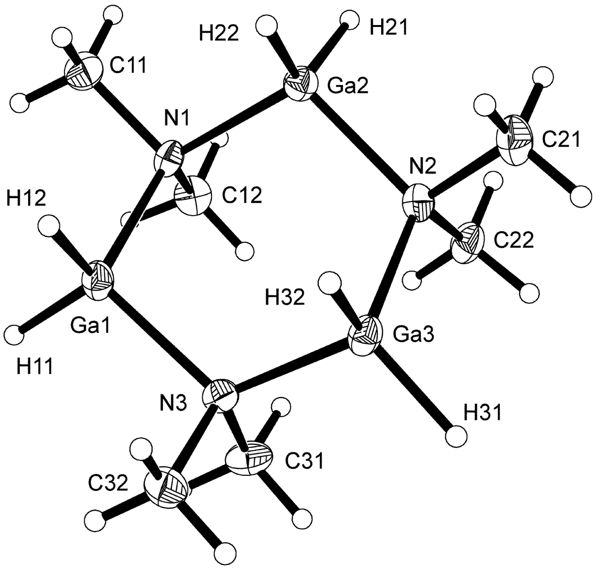

Fig. 5 Structure of solid $[Me_2NGaH_2]_3$ at 150 K as determined by X-ray diffraction.

Crystal structure of dimethylamidogallane at 150 K

The solid decomposition products of the dimethylamine adducts **1** and **2** are comparatively well known,[22,25] but crystallographic data have been reported previously only for the aluminium compound.[25] On the evidence of its IR spectrum and electron-diffraction pattern, the vapour of the gallium compound is composed of dimeric molecules with a cyclic $Ga(\mu\text{-}N)_2Ga$ core and effective D_{2h} symmetry.[22] The vibrational spectra have also been taken to indicate that this dimeric unit is retained in benzene solution and in the solid state. This would be in keeping with the crystal structure of diethylamidogallane,[43] if not with the trimeric molecules which make up the crystal structures of both dimethylamidoalane[25] and gallazane, $[H_2GaNH_2]_3$.[28]

In the event, the structure of crystalline **3** at 150 K is found to consist of the trimeric molecules $[Me_2NGaH_2]_3$ illustrated in Fig. 5. The dimensions of the molecule are listed in Table 4. Dimethylamidogallane is thus completely analogous, at least in the solid phase, to the corresponding alane[25] and to gallazane.[28] The change from trimeric to dimeric units with the replacement of the methyl by ethyl substituents at nitrogen[44] may then be attributed to steric requirements as the non-bonded distances between the substituents on adjacent metal and nitrogen atoms increase as the degree of aggregation is reduced. In truth, the different oligomers are likely to differ but little in energy, as evidenced by the behaviour of **3** on vaporisation, and it is quite conceivable that they should survive in the condensed phases to give more than one solid form. A similarly fine balance is found with alanes and gallanes in which hydrogen fulfils a primary bridging role, *e.g.* $[Me_2AlH]_n$[45] and $[GaBH_6]_n$.[46]

In that the conformation of the $[Me_2NGaH_2]_3$ trimer can be described as predominantly (99%) chair-like with only traces (1%) of boat-like character, it plainly resembles not only

$[Me_2NAlH_2]_3$[25] and $[H_2GaNH_2]_3$,[28] but also the ethyleneimine derivative $[(CH_2)_2NGaH_2]_3$[47] and *cis*-$[Me(H)NAlMe_2]_3$.[48] Alternative conformations are (i) the skew-boat ring favoured by *trans*-$[Me(H)NAlMe_2]_3$,[48] $[(CH_2)_2NAlMe_2]_3$[49] and $[H_2NMMe_2]_3$ (M = Al[50] or Ga[51]), and (ii) the planar ring resulting presumably from the steric bulk of the substituents at aluminium in $[H_2NAlBu^t_2]_3$.[50] The endocyclic N–Ga–N and Ga–N–Ga angles in $[Me_2NGaH_2]_3$ average 108.2 and 114.3°, respectively, very close to the corresponding dimensions of $[Me_2NAlH_2]_3$ (108.8 and 114.9°).[25] The N–Ga–N angle is rather narrower and the Ga–N–Ga angle wider in $[H_2GaNH_2]_3$ (100.3 and 117.1°)[28] and $[(CH_2)_2NGaH_2]_3$ (100 and 116°).[47] At 1.981(3) Å, the average Ga–N distance is identical, within experimental error, with those in $[H_2GaNH_2]_3$,[28] $[(CH_2)_2NGaH_2]_3$,[47] and $[H_2NGaMe_2]_3$,[51] and about 0.05 Å longer than the Al–N distance in comparable alane derivatives with a cyclic $[AlN]_3$ skeleton. Hence the transition from the dimeric $[Me_2NGaH_2]_2$ molecule of the vapour[22] to trimeric $[Me_2NGaH_2]_3$ in the solid is accompanied by a shrinkage of 0.046 Å in the Ga–N distance. This is clearly not consistent with the likely effect of repulsion between the substituents on adjacent metal and nitrogen atoms (see above). In the absence of any obvious correlation between metal–nitrogen distance and ring size, it is quite likely that the contraction of the Ga–N bond arises from enhanced charge transfer in the more polar medium of the solid *versus* the gas phase. Such an effect is commonly found, for example, with adducts like $H_3N{\cdot}BH_3$[27] and $Me_3N{\cdot}GaH_3$.[14] Overall, changes in the coordination number and in the charge distribution at the metal and nitrogen centres, rather than variations of geometry or supposed bond order, appear to be the principal factors determining the metal–nitrogen distances in compounds of this sort.

By neither distance nor angle do the GaH_2 or NMe_2 fragments betray any unusual features. The overall Ga–H distance of 1.51(2) Å is in line with the corresponding distance in other gallane derivatives including $Me_2(H)N{\cdot}GaH_3$ [1.50(3) Å], $Me_3N{\cdot}GaH_3$ [1.51(6) Å],[14] and $[H_2GaNH_2]_3$ [1.56(3) Å],[28] with the last of these having been determined by neutron rather than X-ray diffraction. Between the $[Me_2NGaH_2]_3$ molecules there are no significant contacts to compare with the Ga–H···H–N hydrogen bonds which dominate the intermolecular interactions in the crystalline parent compound $[H_2GaNH_2]_3$ to form a chain parallel to the crystallographic *a* axis.[28] These interactions must account for the marked difference in physical properties of the two compounds: the dimethyl derivative is appreciably more volatile and soluble in non-polar solvents than is the parent compound.

Conclusions

The structures we have determined by X-ray diffraction of single crystals of the compounds dimethylamine–alane, dimethylamine–gallane and dimethylamidogallane at 150 K are noteworthy on three counts.

(i) The dimethylamine adducts each feature dimeric units $Me_2(H)N{\cdot}H_2M(\mu\text{-}H)_2MH_2{\cdot}N(H)Me_2$ with highly unsymmetrical M–H···M hydrogen bridges (M = Al or Ga). While this motif has been encountered previously in other 1 : 1 alane complexes, there is no precedent for it among the crystalline gallane complexes that have been structurally authenticated hitherto. The results appear to show that cleavage of the Ga–H–Ga bridges of digallane has been arrested at a stage not far short of completion.

(ii) Both the dimethylamine adducts show evidence of N–H···H–M interactions between the $[Me_2(H)N{\cdot}MH_3]_2$ units (M = Al or Ga). In the case of the alane, there are single bridges of this kind with H···H distances as short as 1.925(19) Å and N–H···H and Al–H···H angles of 175.9(15) and 139.2(9)°, respectively. By contrast, the bridges of the gallane are bifurcated and appreciably weaker, thereby anticipating the increased reluctance of the compound to eliminate H_2 and metallate the amine fragment.

(iii) In common with the corresponding alane,[25] crystalline dimethylamidogallane is composed of trimeric molecules $[Me_2NGaH_2]_3$ based on cyclic $[GaN]_3$ units with a predominantly chair conformation. Previous studies have shown that vaporisation yields dimeric molecules $[Me_2NGaH_2]_2$.[22] Unlike the parent compound $[H_2GaNH_2]_3$,[28] the *N*-dimethyl derivative gives no hint of significant secondary interactions, a feature reflected in the physical properties of the two compounds and in the way they decompose when heated.

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