698. *Aluminium Hydride Adducts of Trimethylamine: Vibrational Spectra and Structure.*

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The compounds Me_3N,AlH_3, Me_3N,AlD_3, $(Me_3N)_2,AlH_3$, and $(Me_3N)_2,AlD_3$ have been synthesised and their gas-phase infrared spectra recorded in the range 400—4000 cm.$^{-1}$. The Raman spectrum of bistrimethylamine-alane in an excess of trimethylamine has also been studied. The spectra establish that trimethylamine-alane is monomeric (C_{3v} symmetry) and provide cogent evidence for a trigonal-bipyramidal structure (D_{3h}) for the 2 : 1 adduct in which the two ligands occupy the axial positions. Previous assignments of the Al–H and Al–D stretching and deformation modes have been confirmed and the Al–N stretching mode has been identified for the first time. It occurs at 533 cm.$^{-1}$ in the 1 : 1 adduct and, as expected, moves to lower wavenumbers when the second ligand molecule is added, the N–Al–N stretching modes occurring at 460 and 461 cm.$^{-1}$ in the 2 : 1 complex. Ambiguities and inconsistencies in the earlier work on the structure of these compounds have been resolved on the basis of ready equilibration between the components and the possibility of solvent–solute interaction and dipole–dipole association in solution.

THE compounds trimethylamine-alane, Me_3N,AlH_3, and bistrimethylamine-alane, $(Me_3N)_2,AlH_3$, which were first reported by Stecher and Wiberg [1] have been the subject of several studies in recent years.[2-9] However, no unequivocal evidence has been adduced for their molecular complexity and structure. On the basis of molecular-weight determinations in benzene [3,7] it was suggested that the 1 : 1 adduct could dimerise to give 5-coordinate aluminium by means of bridging hydrogen atoms, though there was no spectroscopic evidence for this and others believed the compounds to be essentially monomeric.[4-6]

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[1] Stecher and Wiberg, *Ber.*, 1942, **75**, 2003.
[2] Wiberg, *Z. Naturforsch.*, 1952, **7b**, 578.
[3] Wiberg, Graf, and Uson, *Z. anorg. Chem.*, 1953, **272**, 221.
[4] Zeil, Dautel, and Honsberg, *Z. Elektrochem.*, 1956, **60**, 1131.
[5] Dautel and Zeil, *Z. Elektrochem.*, 1960, **64**, 1234.
[6] Schomberg and Hoffmann, *Z. Elektrochem.*, 1956, **61**, 1110.
[7] Ruff and Hawthorne, *J. Amer. Chem. Soc.*, 1960, **82**, 2141.
[8] Ruff and Hawthorne, *J. Amer. Chem. Soc.*, 1961, **83**, 535.
[9] Davidson and Wartik, *J. Amer. Chem. Soc.*, 1960, **82**, 5506.

The 2 : 1 adduct was originally thought to have a symmetrical trigonal-bipyramidal structure[4] though later work[5,6] showed that aluminium hydride derivatives reacted with some of the solvents used. Dipole-moment measurements[6] were interpreted in terms of an unsymmetrical trigonal-bipyramidal structure in which one of the ligands occupied an equatorial position and apparent support for this structure was obtained from solution spectroscopy. However, the position and even the number of infrared bands observed varied markedly with the solvent.[5,6] A tenous argument has also been advanced in favour of a bridged dimeric structure for the 2 : 1 complex in which the aluminium is 6-co-ordinate.[9]

Amine adducts of gallium hydride were recently shown to have an intense absorption in the infrared region which enables their spectra to be studied at low pressures (1—5 mm.) in the gas phase.[10,11] Preliminary studies showed that the corresponding adducts of aluminium hydride behaved similarly and this enabled the complications mentioned to be avoided by investigating the infrared spectra in the gas phase rather than in solution or in the solid state. Further ambiguities were resolved by following the effects of substitution by deuterium and by studying the Raman spectrum. The results show that the 1 : 1 and the 2 : 1 adduct are both monomeric and have the highest possible symmetry. A complete vibrational assignment has been made for both compounds.

EXPERIMENTAL AND RESULTS

Compounds were handled in a conventional vacuum-line, or in a dry, nitrogen-filled glove box. Solvents were dried over sodium wire or molecular sieve (type 5A) and then distilled from lithium aluminium hydride. Trimethylamine was dried over lithium aluminium hydride and then distilled under reduced pressure at $\sim -50^\circ$.

Trimethylamine-alane was prepared by the reaction[7]

$$LiAlH_4 + Me_3NHCl \xrightarrow[-60^\circ]{Et_2O} Me_3N,AlH_3 + LiCl + H_2$$

The volume of hydrogen evolved was measured by means of a Toepler pump and was equivalent to 1 mol. (found: 237 ml.; required, 226 ml.). The ether was removed at -20°; the product, sublimed into a trap at -40°, had m. p. (sealed tube) 75° (lit.,[7] 76°) (Found: Al, 30·4; active H, 3·5; Me_3N, 64·2. Calc. for Me_3N,AlH_3: Al, 30·3; active H, 3·4; Me_3N, 66·3%).

Trimethylamine-trideuterioalane, Me_3N,AlD_3, was prepared similarly by using 0·397 g. of lithium aluminium deuteride (Metal Hydrides Inc.) and trimethyldeuterioammonium chloride (0·797 g.) in ether (50 ml.). The volume of deuterium evolved was 200 ml. (calc., 190 ml.).

The trimethyldeuterioammonium chloride, Me_3NDCl, was prepared by condensing deuterium chloride on to a large excess of trimethylamine in ether at -196°. The mixture was allowed to warm to -78° for complete reaction. The ether and the excess of trimethylamine were then removed at -40° and final traces of ether removed under a vacuum at 50°. The solid-phase infrared spectra of trimethylammonium chloride and trimethyldeuterioammonium chloride were obtained over the region 400—4000 cm.$^{-1}$ and compared with published spectra for the corresponding iodides.[12] The N–D stretching mode was observed at 2100 cm.$^{-1}$.

Deuterium chloride was prepared[13] by the reaction of deuterium oxide with benzoyl chloride and was purified by fractionation in the vacuum line.

Bistrimethylamine-alane was prepared by condensing trimethylamine (20 ml.) on to finely ground trimethylamine-alane (1·155 g.) at a low temperature. The mixture was warmed to -45° and allowed to react. The excess of trimethylamine was removed at -20°, and the remaining white crystals were sublimed into a trap at -196° in a closed system because it was found that continuous pumping removed trimethylamine vapour to give the 1 : 1 adduct [Found: Al, 18·0; N, 18·7. Calc. for $(Me_3N)_2,AlH_3$: Al, 18·2; N, 18·9%].

Bistrimethylamine-trideuterioalane was prepared similarly from trimethylamine-trideuterioalane and an excess of trimethylamine.

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[10] Greenwood, Storr, and Wallbridge, *Proc. Chem. Soc.*, 1962, 249.

[11] Greenwood, Storr, and Wallbridge, *Inorg. Chem.*, 1963, **2**, in the press.

[12] Ebsworth and Sheppard, *Spectrochim. Acta*, 1959, **13**, 261.

[13] Brown and Groot, *J. Amer. Chem. Soc.*, 1942, **64**, 2223.

Analytical Methods.—Active hydrogen was determined gas-volumetrically after solvolysis with de-aerated methanol. The trimethylamine so liberated was passed into an excess of hydrochloric acid and determined by back-titration. Nitrogen was also determined independently by the Kjeldahl method and aluminium by means of 8-hydroxyquinoline.

TABLE 1.

Infrared absorption bands (cm.$^{-1}$) of trimethylamine-alane and -trideuterioalane.

Me_3N,AlH_3	Me_3N,AlD_3	Assignment
1792	1304	ν_1, ν_4 sym. and antisym. Al–H stretch
773	567	ν_5 antisym. H–Al–H deformation
768	562	ν_2 sym. H–Al–H deformation
533	~540	ν_3 Al–N stretch

TABLE 2.

Raman and infrared absorption bands (cm.$^{-1}$) of bistrimethylamine-alane and the infrared absorption bands of bistrimethylamine-trideuterioalane.

$(Me_3N)_2,AlH_3$		$(Me_3N)_2,AlD_3$	
Raman	Infrared	Infrared	Assignment
1728	†	†	ν_1 sym. Al–H stretch
1710	1709	1246	ν_5 antisym. Al–H stretch
*	895	645	ν_3 $Al\equiv H_3$ out-of-plane bend
764	790	607	ν_6 $Al\equiv H_3$ in-plane bend
724	727	542	ν_8 N–Al–H bend
*	460	460	ν_4 N–Al–N antisym. stretch
461	†	†	ν_2 N–Al–N sym. stretch
‡	‡	‡	ν_7 N–Al–N bend

* Inactive in Raman. † Inactive in infrared. ‡ Unobserved, but expected at low frequencies in both the Raman and the infrared spectrum.

Spectra.—Gas-phase infrared spectra were determined in the region 400—4000 cm.$^{-1}$ by means of a Perkin-Elmer model 137 Infracord spectrophotometer with sodium chloride optics and a model 137 KBr Infracord instrument. The gas cell was 10 cm. long and was fitted with a side arm into which the compounds could be sublimed. The results are shown in Tables 1 and 2 which record only those lines which appear in addition to those of the parent ligand trimethylamine (see also Fig. 2).

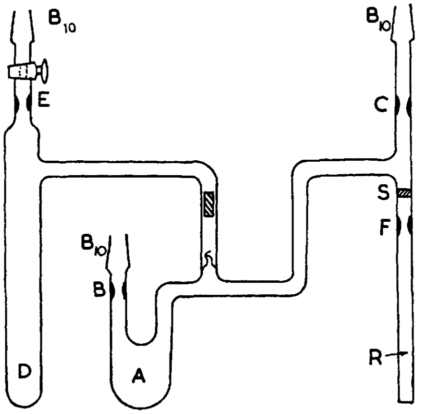

FIG. 1. Apparatus for preparation of Raman samples.

The Raman spectrum of bistrimethylamine-alane in an excess of trimethylamine (sample volume 7 ml.) was determined with mercury 4358 Å excitation and a Toronto-arc source coupled to a Hilger E612 spectrograph, photomultiplier, and photoelectrically driven pen-recorder. A saturated solution of potassium nitrite was used as optical filter. Frequencies were correct within ±2 cm.$^{-1}$ for sharp lines but were perhaps less accurate for weaker or broader bands. The results are recorded in Table 2 which lists those lines not present in the Raman spectrum of trimethylamine itself.

Preparation of Raman Samples.—Pure trimethylamine-alane was prepared and sublimed under a dynamic vacuum into bulb A of the all-glass apparatus shown in Fig. 1; this was then sealed at B and C. Trimethylamine, dried by repeated vacuum-distillations over lithium aluminium hydride and a final distillation from bistrimethylamine-alane, was condensed into the tube D which was then sealed at E. The trimethylamine was next condensed on to the complex *via* the break-seal, and the solution was allowed to warm to room temperature; it was then passed through the sinter S by cooling the Raman tube R and allowing the pressure of trimethylamine in A to force the liquid into the Raman tube which was finally sealed at constriction F.

DISCUSSION

When trimethylamine-alane is freshly prepared and allowed to warm to room temperature the vapour pressure above the solid is ~2—3 mm. The infrared spectrum of this gas (Fig. 2a) contains nine bands in addition to those attributable to the trimethylamine residue, but these bands are not derived from a single compound since they form two well-defined sets. During 12 hours the four intense bands listed in Table 1 diminish in intensity and almost disappear, whilst the five infrared bands listed in Table 2, which were originally weak, become considerably stronger. Detailed measurements show that, in each set, the rate of decay or growth of all bands is the same. At the end of the 12-hour period the cell contained a gas which was non-condensable at —196° (presumably hydrogen) and trimethylamine (identified by its vapour pressure and infrared spectrum). These

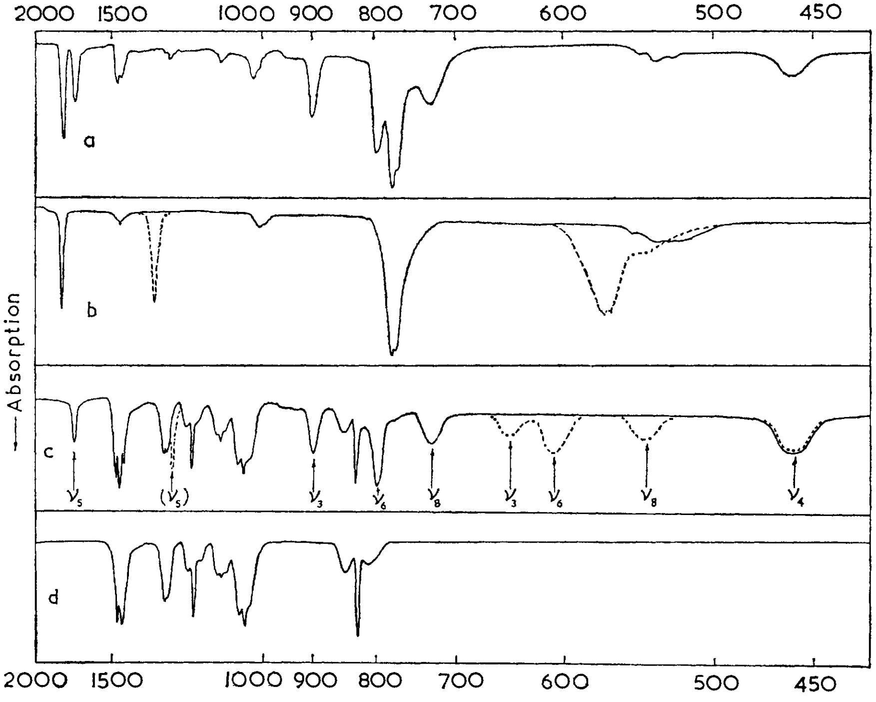

FIG. 2. Gas-phase infrared spectra:

(a) Mixture of Me_3N,AlH_3 and $(Me_3N)_2,AlH_3$.
(b) (——) Me_3N,AlH_3, (- - -) Me_3N,AlD_3.
(c) (——) $(Me_3N)_2,AlH_3$, (- - -) $(Me_3N)_2,AlD_3$ plus excess of Me_3N.
(d) Me_3N.

observations suggest that trimethylamine-alane slowly dissociates in the gas phase and that equilibration in the vapour between the 1 : 1 and 2 : 1 adducts occurs readily:

$$\mathrm{Me_3N,AlH_3} \longrightarrow \mathrm{Me_3N} + [\mathrm{AlH_3}]$$

$$\mathrm{Me_3N,AlH_3} + \mathrm{Me_3N} \rightleftharpoons (\mathrm{Me_3N})_2,\mathrm{AlH_3}$$

The " polymeric aluminium hydride " formed as a white powder in the gas cell decomposes gradually into aluminium and hydrogen. Over longer periods the bands attributed to bistrimethylamine-alane themselves slowly diminish in intensity owing to the dissociation of the 2 : 1 adduct as above. There is thus a continuous process over a period of weeks which results ultimately in complete decomposition of the adduct into free trimethylamine and " polymeric aluminium hydride " which itself subsequently undergoes partial decomposition. The process is accelerated at higher temperatures, and experiments with heated gas cells 20—70° indicated that the 2 : 1 complex becomes increasingly unstable with respect to dissociation into the 1 : 1 complex. Similar equilibria have recently been postulated [14] to explain observations on the vapour pressure of this system. It is important to distinguish this behaviour in the vapour phase from dissociation equilibria involving the solid adduct and gaseous trimethylamine.[8]

The infrared spectrum of the pure 1 : 1 adduct uncontaminated with 2 : 1 adduct is difficult to obtain in the gas phase because of the equilibrium discussed in the preceding paragraph. However, spectra can be obtained which show only minute traces of the 2 : 1 adduct by briefly evacuating the gas cell and recording the spectrum of the freshly evaporated compound. The spectrum shown in Fig. 2b and Table 1 was obtained in this way.

Bistrimethylamine-alane vapour is stable only in the presence of excess of trimethylamine gas and the spectrum of this compound, uncontaminated with 1 : 1 complex, was obtained by condensing an excess of trimethylamine on to a sample of the 1 : 1 adduct in the gas cell (see Fig. 2c). Brief evacuation of the cell to remove most of the excess of trimethylamine produced a spectrum of the mixture again, similar to that in Fig. 2a, and a further series of evacuations increased the proportion of the 1 : 1 adduct until almost all the 1 : 2 adduct had dissociated and the spectrum approached that shown in Fig. 2b. When the isolated cell was put aside at this stage, the proportion of 2 : 1 adduct in the gas phase increased spontaneously to a maximum and then gradually diminished as a result of the equilibria discussed above.

The structure of gaseous trimethylamine-alane at about 3 mm. can be determined from a consideration of the four observed bands, the effects of deuteration on the positions of these bands, and by direct comparison with the spectrum and assignments of trimethylamine-gallane.[10,11] The four bands listed in Table 1 can be assigned to the tetrahedral $\mathrm{N{\rightarrow}AlH_3}$ group, and the assignments shown are consistent with a monomeric C_{3v} structure; this requires a maximum of six infrared-active bands, of which five shift on deuteration. The fact that only four bands are observed can be interpreted on the basis of the expected degeneracy of the ν_1 and ν_4 Al–H stretching modes [11] and the fact that the $\mathrm{N{-}Al{\equiv}H_3}$ bending mode, ν_6, is expected to give the weakest band.[11] In view of the necessarily low pressure at which the gas-phase spectrum was recorded and the observed low intensity of the next strongest band (ν_3, see Fig. 2b) it seems likely that this band was too weak to be observed. In fact, only one band was observed below 600 cm.$^{-1}$ and this has been assigned to the Al–N stretching mode. This band does not move on deuteration and its position at 533 cm.$^{-1}$ ($\sim$540 cm.$^{-1}$ in the deuterio-complex) corresponds closely to the value of 541 cm.$^{-1}$ calculated on the basis of a change of mass from the band at 482 cm.$^{-1}$ in the spectrum of trimethylamine-gallane; the latter band has been unequivocally assigned to the Ga–N mode on the basis of its well defined *PQR* structure and its invariance on deuteration.[10,11] The *PQR* structure was also discernible for the alane adduct and the

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[14] Heitsch, *Nature*, 1962, **195**, 995.

separation of the *P* and the *R* branch (~24 cm.$^{-1}$) agrees well with the value of 23 cm.$^{-1}$ calculated in the usual way.[15]

The only other feature of interest in the spectra of the 1 : 1 adduct is the position of the weak band at 1005 cm.$^{-1}$, derived from the C–N antisymmetric stretch of trimethylamine which occurs at 1040 cm.$^{-1}$ in the free ligand. The shift of 35 cm.$^{-1}$ is the largest observed for any of the trimethylamine bands and is not unexpected since involvement of the nitrogen atom in the donor–acceptor bonding is likely to weaken the C–N bond.

The foregoing discussion establishes that pure trimethylamine-alane has an extremely simple spectrum in the gas phase, and the more complicated spectra observed both in the gas phase and in solution arise from the presence of the 2 : 1 adduct as impurity. There is no evidence for a dimeric structure in the gas phase since the highest possible symmetry for this is D_{2h} which requires eleven infrared-active modes; the observed spectrum is much simpler than this and this is no indication of any Al–H–Al stretching or deformation mode.

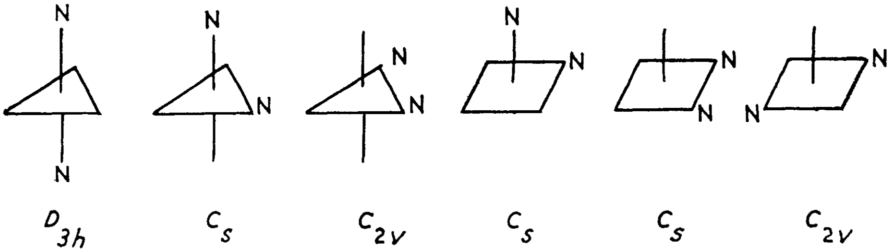

FIG. 3. Possible symmetries for bistrimethylamine-alane.

D_{3h}: $2a_1'$ (R); $2a_2''$ (I); $3e'$ (R, I); $1e''$ (R); *i.e.*, 6R, 5I, 3-coincidences.
C_{2v}: $5a_1$ (R, I); $1a_2$ (R); $3b$ (R, I); $3b_2$ (R, I); *i.e.*, 12R, 11I, 11 coincidences.
C_s: $8a'$ (R, I); $4a''$ (R, I); *i.e.*, 12R, 12I, 12 coincidences.
Observed: 5R, 5I, 3 coincidences.

Indeed the bands in both the 1 : 1 and the 2 : 1 complex are particularly sharp and most have half-band widths within the range 15—20 cm.$^{-1}$.

The structure of gaseous bistrimethylamine-alane in the presence of an excess of trimethylamine vapour cannot be determined by infrared spectroscopy alone, and supplementary Raman data were therefore obtained. If the compound is considered to be monomeric, the aluminium atom must be 5-co-ordinate and various structures based on the trigonal bipyramid and the square-based pyramid are possible (see Fig. 3). According to the selection rules, the infrared spectrum of all the structures except D_{3h} would be expected to exhibit eleven (C_{2v}) or twelve (C_s) fundamental bands. By contrast, the D_{3h} structure has only five allowed fundamentals in the infrared region ($2a_2'' + 3e'$), and six allowed fundamentals in the Raman spectrum [$2a_1'$(pol) + $3e'$(depol) + $1e''$(depol)] with three coincidences. A dimeric structure for the 2 : 1 adduct in which the molecules are connected by hydrogen bridges whould exhibit at least 13 infrared bands and 15 Raman bands according to the selection rules for a D_{2h} structure (the highest possible symmetry for the dimer). Since, as shown in Table 2, five infrared bands and five Raman lines with three coincidences are observed for bistrimethylamine-alane in the region 400—4000 cm.$^{-1}$, D_{3h} symmetry is highly probable both in the vapour phase and in trimethylamine solution. This conclusion is borne out by the effects of deuteration on the position of the bands and establishes the 2 : 1 complex as the first authenticated example of 5-co-ordinate aluminium.

The Raman spectrum shows two bands in the 1700 cm.$^{-1}$ region and one of the bands is coincident with the infrared band at 1709 cm.$^{-1}$. The coincident band can thus be

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[15] Gerhard and Dennison, *Phys. Rev.*, 1933, **43**, 197.

assigned to the antisymmetric Al–H stretch ν_5, while the other band must be the Al–H symmetric stretch ν_1 which is only active in the Raman. The N–Al–N stretching modes ν_2 and ν_4 are expected in the 400—500 cm.$^{-1}$ region by comparison with the assignment for the Al–N stretch in the 1 : 1 adduct. Bands at 461 and 460 cm.$^{-1}$ appear in the Raman and infrared spectra and these bands have therefore been assigned to the symmetric ν_2 and the antisymmetric ν_4 stretching mode, respectively, the near coincidence in frequency being fortuitous. These assignments are confirmed by the infrared spectrum of bistrimethylamine-trideuterioalane: the band at 1709 cm.$^{-1}$ is shifted by the expected amount to 1246 cm.$^{-1}$, whereas the band at 460 cm.$^{-1}$ remains unchanged since it does not involve motion of the hydrogen atoms.

The three sharp bands between 700—900 cm.$^{-1}$ arise from the bending modes ν_3, ν_6, and ν_8. The Al≡H_3 out-of-plane bend ν_3 is in the A_2'' symmetry class and will therefore be active only in the infrared region. The band at 895 cm.$^{-1}$ was observed only in the infrared spectrum and is therefore assigned to this mode. The suggestion that it may be an extra N–C mode [6] is untenable since it moves the expected amount to 645 cm.$^{-1}$ on deuteration. It should be possible to distinguish between the two remaining modes ν_6 and ν_8 provided that the trimethylamine ligands produce no deviation from local D_{3h} symmetry about the aluminium atom. In this case the rigid selection rules would predict that the in-plane bend ν_6 would be active both in the infrared and the Raman spectrum, whilst the N–Al–H bend ν_8 would be active only in the Raman spectrum. In fact, the observed infrared and Raman spectra suggest the possible occurrence of two coincidences in this region. It is not unreasonable to expect some violation of the rigid selection rules in a molecule such as the 2 : 1 adduct since, although the aluminium atom is essentially surrounded by a trigonal bipyramid of three hydrogen atoms and two nitrogen atoms with D_{3h} symmetry, the methyl groups attached to the nitrogen atoms could well modify the local symmetry depending on their relative orientations. This modification in local site symmetry could be sufficient to enable the ν_8 mode to be observed in the infrared as well as in the Raman spectrum. The N–Al–H bending mode ν_8 is assigned to the band at 727 cm.$^{-1}$ since this deformation would probably require less energy than the Al≡H_3 in-plane bending mode ν_6. Both bands move the expected amount on deuteration, and this excludes an earlier suggestion [4] that the band at 727 cm.$^{-1}$ belongs to the N–Al–N stretching mode.

The N–Al–N bending mode ν_7 should appear below the N–Al–N stretching modes at 460—461 cm.$^{-1}$ and is expected to be active, though weak, in both the infrared and the Raman spectrum. The infrared spectrum was not investigated below 400 cm.$^{-1}$ and observation on the Raman spectrum in this region was difficult because of the high background. The ν_7 mode, therefore, does not occur in the assignments listed in Table 2. In summary, the overall assignments are consistent with a symmetrical trigonal-bipyramidal structure for bistrimethylamine-alane both in the gas phase and in trimethylamine solution. All other structures have lower symmetry and are considered to be much less likely in view of the simplicity of the observed spectra. The derived structure is also consistent with the stability sequence obtained for 2 : 1 adducts of aluminium hydride with a series of tertiary amines.[8]

Several works [4–6] have examined the infrared spectra of trimethylamine-alane and bistrimethylamine-alane in various solvents. These spectra have now been re-investigated with benzene as a solvent and the results suggest that the ready equilibrium which exists between the 1 : 1 and 2 : 1 adducts in the gas phase is also present in solution. The spectra obtained by dissolving the pure 1 : 1 adduct in benzene always contained some bands which could be ascribed to the 2 : 1 adduct, by comparison with the gas-phase spectrum of this compound. The spectrum of the 2 : 1 adduct in benzene showed only very weak additional bands due to the 1 : 1 adduct, but again it was evident that a dissociation equilibrium was occurring.

In view of the difficulty of carrying out physical measurements on the pure compounds without contamination from the related adduct it appears likely that the dipole moment of 1·2—1·3 D reported for bistrimethylamine-alane[6] is due to partial dissociation of the 2 : 1 adduct into trimethylamine-alane for which a dipole moment of about 5 D is expected, and free trimethylamine ($\mu = 0{\cdot}67$ D). The ready disproportionation of the 1 : 1 complex could also account, in part, for the high molecular weight of the 1 : 1 adduct in benzene,[3,7] though this may also be due to weak dipole–dipole association about the co-ordinate bond $N^+–Al^-$ which would be sufficient to affect the colligative properties without seriously modifying the spectra.

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