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Gallane: Synthesis, Physical and Chemical Properties, and Structure of the Gaseous Molecule Ga_2H_6 As Determined by Electron Diffraction

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Abstract: The elusive binary hydride of gallium, $[GaH_3]_n$, has at last been synthesized in rigorously conditioned all-glass apparatus by the reaction between monochlorogallane, $[H_2GaCl]_2$, and lithium tetrahydridogallate, $LiGaH_4$, near −30 °C. The compound, which decomposes to the elements at ambient temperatures, has been characterized by chemical analysis, by its vibrational and ^1H NMR spectra, and by chemical trapping with trimethylamine. The infrared spectra of the vapor species at low pressures (sampled directly at ambient temperatures or trapped in a solid inert matrix at ca. 20 K, and including the results of deuteration experiments) leave little doubt that the principal component is the diborane-like molecule $H_2Ga(\mu\text{-}H)_2GaH_2$. Such a conclusion is endorsed by electron-diffraction measurements, carried out on the vapor at ca. 255 K; these are consistent with an r_a structure featuring the following parameters: $r(Ga\cdots Ga)$ 258.0 (0.2), $r(Ga\text{-}H_t)$ 151.9 (3.5), and $r(Ga\text{-}H_b)$ 171.0 (3.8) pm; and $\angle Ga\text{-}H_b\text{-}Ga$ 97.9 (3.2)° (H_t = terminal H atom; H_b = bridging H atom). The molecule Ga_2H_6 is highly susceptible to aggregation. The vibrational spectra of the solid suggest the presence of an oligomer $[GaH_3]_n$ where $n > 2$ and possibly equal to 4, but still retaining terminal Ga–H bonds (cf. α-AlH_3). A similar species is probably a major constituent of toluene-d_8 solutions of the gallane; at temperatures <−30 °C, such a solution displays two distinct ^1H magnetic resonances with relative intensities 2:1 attributable to H_t and H_b atoms. The reactions of gallane appear mostly to parallel those of diborane. Thus, symmetrical cleavage of the $Ga(\mu\text{-}H)Ga$ bridges occurs with NMe_3 (at −95 °C) or PH_3 (under matrix-isolation conditions) to give the corresponding molecular adduct L_nGaH_3 ($L = NMe_3$, n = 1 or 2; $L = PH_3$, n = 1), whereas NH_3 causes unsymmetrical cleavage at −95 °C with the formation of $[H_2Ga(NH_3)_4]^+GaH_4^-$. Quantitative metathesis with HCl brings about Ga–H/Ga–Cl exchange with the production of H_2, while stepwise insertion into the Ga–H bonds is the path taken by the reaction with C_2H_4, affording Ga–Et derivatives.

The hydrides of boron represent familiar and intensively researched territory,[2] and aluminum hydride, $[AlH_3]_n$, is also comparatively well authenticated,[3a] the solid α-form being isostructural with AlF_3 and featuring six-coordinate aluminum atoms.[3b] By contrast, the uncoordinated binary hydride of gallium has been for many years something of a will-o'-the-wisp, if one discounts the vapor-phase transients GaH[4a] and GaH_3[4b] formed at high temperatures. As early as 1941 Wiberg et al. described the synthesis of the free hydride via two routes:[5]

$$GaCl_3 + LiMH_4 \xrightarrow{\text{ether}} (1/n)[GaH_3]_n + LiMCl_3H \quad (1)$$
$$(M = Al \text{ or } Ga)$$

$$(6/n)[Me_2GaH]_n + 4Et_3N \rightarrow 4Et_3N\cdot GaMe_3 + Ga_2H_6 \quad (2)$$

but subsequent investigations[6a] were unable to verify these reports. On the other hand, 1963 witnessed the presentation of analytical and spectroscopic evidence[6b] for the low-temperature displacement reaction:

$$Me_3N\cdot GaH_3(c) + BF_3(g) \xrightarrow{-15\ °C} (1/n)[GaH_3]_n(l) + Me_3N\cdot BF_3(c) \quad (3)$$

which is still widely accepted as a route to uncoordinated gallane.[6c] Yet, on the evidence of mass-spectrometric and matrix-isolation studies,[7,8] the vapor species derived from the interaction of $Me_3N\cdot GaH_3$ with BF_3 include B_2H_6 and BH_nF_{3-n} species in proportions implying that *halide–hydride exchange*, and not displacement, is the predominant reaction pathway. Amid such vicissitudes, there must be serious reservations about claims made prior to 1989 regarding the synthesis of anything approaching pure, well-characterized samples of gallane itself.

Earlier attempts to prepare gallane in this laboratory[8] compassed a variety of potential routes, viz., (i) displacement reactions involving an adduct of GaH_3, e.g., $Me_3N\cdot GaH_3$ or $NaGaH_4$, and an acid, e.g., BF_3 or HCl; (ii) gas-phase pyrolysis or matrix photolysis of an adduct of GaH_3; and (iii) the interaction of a tetrahydridogallate $MGaH_4$ (M = Li or Na) with a gallium compound, e.g., $GaCl_3$. The only one of these to give any encouragement was the interaction of gallium(III) chloride with a tetrahydridogallate, the solid mixture yielding under solvent-free conditions at ambient temperatures small amounts (in the order of 1 mg or less) of a volatile, thermally unstable product, in addition to substantial quantities of elemental gallium and hydrogen. The condensate formed by quenching the vapor of the

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(8) Baxter, P. L. D.Phil. Thesis, University of Oxford, 1984. Goode, M. J. D.Phil. Thesis, University of Oxford, 1987. Experiments carried out in Oxford, unlike those reported in ref 7, yielded a product answering to the description of the material alleged in ref 6b to be uncoordinated gallane. Closer scrutiny, allied to studies of chloride–fluoride exchange reactions of the chlorogallane $[H_2GaCl]_2$, gives us to believe that the material is a mixture of fluorogallanes of the type $[H_xGaF_{3-x}]_n$, where x = 1 or 2 and $n \geq 2$ (Baxter, P. L.; Downs, A. J.; Goode, M. J.; Pulham, C. R. Unpublished results).

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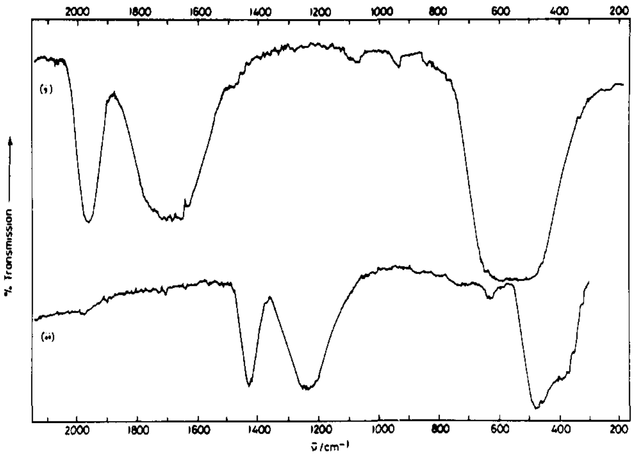
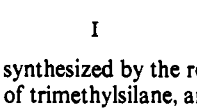


Figure 1. The IR spectrum of the annealed solid film formed by condensing the volatile products of the reaction between solid gallium(III) chloride and (i) $NaGaH_4$ or (ii) $NaGaD_4$ on a CsI window held at 77 K.

product on a CsI window held at 77 K was typically characterized by the IR spectrum reproduced in Figure 1, with three main absorptions at 1978 (s), 1705 (s, br), and 550 cm^{-1} (s, vbr).[9] The spectrum differs significantly from the one reported by Greenwood and Wallbridge[6b] for the product they identified as free gallane in that it includes a prominent, broad absorption near 1700 cm^{-1}, as well as the much sharper feature near 1980 cm^{-1}. The vibrational properties of compounds containing terminal Ga–H bonds, e.g., $[HGaCl_2]_2$[10] and $[H_2GaCl]_2$,[11] and of dimethylgallane, $[Me_2GaH]_n$, in which hydrogen bridges the gallium atoms in different oligomeric forms,[12] suggests that the bands at 1978 and 1705 cm^{-1} represent $\nu(Ga-H_t)$ and $\nu(Ga-H_b)$ fundamentals, respectively, in an aggregate with a comparatively wide Ga–H–Ga bond angle ($\geq 120°$).[12,13] Irrespective of the conditions of the experiment (including factors like the temperature, residence time, and proportions of the reaction mixture), however, it proved impossible to isolate a product which was entirely free from chloride. Thus, chemical analysis showed that proportion Ga:Cl to be typically $\geq 5:1$, and the ^1H NMR spectrum of toluene-d_8 solutions at low temperatures confirmed that the product contained more than one gallium hydride derivative. It appears, therefore, that a hydride-rich product including species like $[GaH_3]_n$ and $[H_2GaCl]_2$[11] is formed through the interaction of neat gallium(III) chloride and a tetrahydridogallate, but only in very low yields (<1%) and offering little prospect for the isolation of the pure binary hydride, $[GaH_3]_n$.[8]

Altogether superior to gallium(III) chloride as a precursor to gallane is monochlorogallane, $[H_2GaCl]_2$ (I), a compound conveniently synthesized by the reaction of gallium(III) chloride with an excess of trimethylsilane, and which we have now characterized in some detail.[11] Not only is reduction of the gallium already two-thirds complete, but I is also a liquid even at quite low temperatures, and therefore susceptible to more efficient mixing with a hydride ion source like $LiGaH_4$. Indeed, we find that I reacts in vacuo with freshly prepared lithium tetrahydridogallate at −30 to −23 °C to give a volatile product, shown to be gallane, typically in yields of 5–15% based on eq 4.



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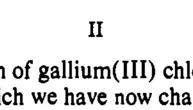

II

$$(\tfrac{1}{2})[H_2GaCl]_2 + LiGaH_4 \xrightarrow{-30\ °C} (1/n)[GaH_3]_n + LiGaH_3Cl \quad (4)$$

As reported briefly in a preliminary communication,[14] the gallane has been authenticated chemically and by its vibrational and ^1H NMR spectra. The results argue for a dimeric molecule Ga_2H_6 with a diborane-like structure II as the predominant vapor species at low pressures, and the IR spectra of the normal and perdeuterated isotopomers have been interpreted on this basis. Such a structure has now been endorsed by an analysis of the electron-diffraction pattern of the vapor at ca. 255 K. Facile aggregation of the Ga_2H_6 molecules occurs in the condensed phases to give a higher oligomer $[GaH_3]_n$, possibly with $n = 4$, with a change in the mode of hydrogen-bridging; in this form, the hydride decomposes rapidly at temperatures in excess of 253 K. Chemical exploration has established that, in its reactions with the bases NH_3, NMe_3, and PH_3, with the unsaturated hydrocarbon C_2H_4, and with the proton source HCl, gallane has much in common with diborane.[2] In this paper we are concerned primarily with the synthesis and physical and chemical properties of gallane; details of the rovibrational transitions now being studied under high resolution in the IR spectrum of the gaseous Ga_2H_6 and $Ga_2H_nD_{6-n}$ molecules will be treated separately.[15] Our preliminary account[14] has stimulated a number of theoretical enquiries in which ab initio MO methods have been exploited to calculate the equilibrium molecular structures, vibrational properties, and binding energies of the molecules Al_2H_6 and Ga_2H_6.[16] In a practical context, too, gallane is potentially important, not only as a means of vapor transport of gallium at low temperatures (<−20 °C), but also as an intermediate in the complex thermolysis reactions attending chemical vapor deposition and terminating in solid gallium-bearing films.[17]

Results and Discussion

(i) **Synthesis of Gallane.** Gallane, $[GaH_3]_n$, has been synthesized by the reaction in vacuo of monochlorogallane, $[H_2GaCl]_2$, with lithium tetrahydridogallate, $LiGaH_4$, under solvent-free conditions, each of the reagents being freshly prepared.[11,18] The choice of hydride ion source is dictated by its activity and by the need to avoid the formation of mixed hydride derivatives; thus, lithium tetrahydridoaluminate is less efficient in this role than the tetrahydridogallate, and lithium tetrahydridoborate gives high yields of gallaborane, $H_2Ga(\mu\text{-}H)_2BH_2$.[19] After co-condensation of the monochlorogallane with the tetrahydridogallate, the reaction is initiated by allowing the mixture to warm to ca. −23 °C. The volatile products removed under continuous pumping comprise, in addition to substantial quantities of elemental hydrogen, a significant yield of condensable material. The principal, sometimes sole, component of this material is a homogeneous, volatile product

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(9) s strong, m medium, w weak, br broad, v very.

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Table I. Vibrational Spectra of Annealed Solid Films of Gallane (200–4000 cm^{-1}) at ca. 77 K

IR spectrum						Raman spectrum				
$[GaH_3]_n$[a]		$[GaD_3]_n$[a]				$[GaH_3]_n$		$[GaD_3]_n$		
$\tilde{\nu}/cm^{-1}$	intens[b]	$\tilde{\nu}/cm^{-1}$	intens[b]	$\tilde{\nu}_H/\tilde{\nu}_D$	assignment[b]	$\tilde{\nu}/cm^{-1}$	intens[b]	$\tilde{\nu}/cm^{-1}$	intens[b]	$\tilde{\nu}_H/\tilde{\nu}_D$
1978	s	1422	s	1.39	$\nu(Ga-H_t)$	1977	s	1412	s	1.40
1705	s, br	1200	s, br	1.42	antisym $\nu(Ga-H_b)$	*c*		*c*		
1100	vw				2 × ca. 550					
950	vw	~720	vw, br?	1.32	sym $\nu(Ga-H_b)$	*c*		*c*		
		625	w, br		$[GaHD_2]_n$ impurity					
550	s, vbr	400	s, br	1.38	$Ga-H_t$ deformation modes	700	w, br	500	w, br	1.40
						520	w, br	375	w, br	1.39

[a] An IR spectrum essentially similar to this is observed for samples of Ga_2H_6 or Ga_2D_6 isolated in an Ar, Kr, or N_2 matrix *after annealing* the deposit at temperatures ≥30 K. [b] s strong, w weak, v very, br broad, t terminal, b bridging. [c] No Raman scattering attributable to $\nu(Ga-H_b)$ modes was observed. The Raman spectrum of solid $[Me_2GaH]_n$, which probably has a structure similar to that of $[GaH_3]_n$ with $Ga-H_b-Ga$ bridges, is also devoid of any bands in this region (Baxter, P. L. D.Phil. Thesis, University of Oxford, 1984). Hence it seems that $\nu(Ga-H_b)$ modes have a low cross-section with respect to Raman scattering, reflecting presumably the polarity of the $Ga-H_b$ linkage.

which can be isolated by fractional condensation in vacuo and which, on the evidence of chemical and spectroscopic analysis (q.v.), is essentially pure gallane. The condensable material often includes a second fraction, typically inhomogeneous and consisting of chlorogallanes like Ga_2H_5Cl and unchanged $[H_2GaCl]_2$; unlike gallane, this does not have an appreciable vapor pressure at −45 °C, and the distillation properties admit comparatively easy and clean separation of the two fractions. Gallane can thus be generated in yields varying between 5 and 15% based on the quantity of monochlorogallane consumed in accordance with eq 4, and depending chiefly on the precise state and purity of the lithium tetrahydridogallate. That the initially white reaction mixture is observed to turn dark gray during the course of the reaction signals presumably the formation of elemental gallium. Gray deposits of elemental gallium are likely also to appear on the walls of the apparatus unless steps are taken to maintain adequate control of the temperature.

To achieve success with the synthesis and manipulation of gallane demands scrupulous attention to practical technique. Two prerequisites are of crucial importance. Firstly, it is imperative *rigorously* to exclude moisture, grease, or other contaminants, to an extent which has necessitated the development of appropriate vacuum-line procedures. Operations must be carried out at pressures $<10^{-4}$ mmHg *in all-glass apparatus* designed to give short distillation paths and which has been preconditioned by heating under continuous pumping. Gallane vapor does not survive the passage through either greased or greaseless valves which cannot be adequately conditioned in this way. Instead a trap must normally be equipped (i) with constrictions to permit isolation of a sample by sealing under vacuum and (ii) with a break-seal permitting access to the sample to be regained under equally rigorous conditions. Secondly, the thermal frailty of gallane requires that all glassware to which it has access must be maintained at temperatures <−10 °C. Even so, the properties of gallane impose severe limitations on what can be realistically achieved by way of physical and chemical characterization. Thus, the proclivity to decompose or react with adventitious impurities tends to thwart a variety of potentially informative studies involving, for example, the use of Raman, ^1H NMR, or mass-spectrometric techniques to interrogate the vapor species. Further practical details are given in the Experimental Section.

Efforts to improve the yield of gallane by using a solvent to moderate the reaction have so far enjoyed only limited success. The choice of medium is obviously restricted by the need to minimize both basic properties (which might make it difficult to free the gallane from the solvent) and the susceptibility to reduction. With *n*-octane as the reaction medium, the gallane can be separated from the solvent without undue difficulty, but without any benefit to the yield. Methylcyclohexane offers still less advantage, with the gallane formed in low yield and defying attempts to free it from the solvent. By contrast, toluene has the capacity to improve the yield (up to 60%), but fractional condensation gives only small quantities of pure gallane, the bulk of the product remaining with the solvent-rich fraction. Such drawbacks apart, this approach may yet provide a useful route to toluene solutions of the gallane.

Gallane condenses at low temperatures as a white solid which melts at ca. −50 °C to form a colorless, viscous liquid. The rate of vaporization of the solid at −63 °C is consistent with a vapor pressure in the order of 1 mmHg. Samples of the material in the condensed phase (liquid or solution) decompose to the elements at temperatures in excess of −30 °C. At a pressure of 10 mmHg the vapor has a half-life of about 2 min at ambient temperatures.

(ii) **Chemical Analysis.** Gallane decomposes to the elements at ambient temperatures in accordance with eq 5, although competition from side-reactions with traces of adsorbed moisture or other hydroxylic impurities (as in eq 6) make this a less than ideal method of quantitative analysis for small amounts of the material (≤5 mg).

$$(1/n)[GaH_3]_n \rightarrow Ga + \tfrac{3}{2}H_2 \qquad (5)$$

$$Ga-H + H_2O \rightarrow Ga-OH + H_2 \qquad (6)$$

On the other hand, qualitative and quantitative analyses for chlorine confirm that the compound can be made free from contamination by chlorogallanes. Moreover, quantitative assay establishes that the reaction with an excess of anhydrous hydrogen chloride at −95 °C proceeds in accordance with eq 7, and thereby offers a satisfactory means of analysis of the gallane.

$$(1/n)[GaH_3]_n + 3HCl \rightarrow \tfrac{1}{2}Ga_2Cl_6 + 3H_2 \qquad (7)$$

(iii) **Vibrational Spectra.** IR spectra have been measured for isotopically normal and perdeuterated versions of gallane, with reference to the vapor at low pressures (≤10 mmHg) and ambient temperatures, to the vapor species trapped in a solid argon, krypton, or nitrogen matrix at ca. 20 K, and to the annealed solid condensate formed on a CsI window at 77 K. Raman spectra have also been measured for the solid condensate formed on a copper block at 77 K; attempts to carry out such measurements on toluene solutions of the gallane at ca. 200 K revealed only two bands attributable to the solute (at 1958 and 1972 cm^{-1}), being thwarted mainly by the low scattering cross-section of this species. Selected spectra are illustrated in Figures 2 and 3, and the details itemized in Tables I and II. Wavenumbers quoted in parentheses in the ensuing discussion refer to the corresponding perdeuterated compound.

The first point to note is that a film of the annealed solid compound at 77 K displays an IR spectrum resembling that of the condensate formed by the vapors derived from the reaction of an excess of metal tetrahydridogallate with gallium(III) chloride (compare Figures 1 and 2 and Table I). The three main absorptions at 1978, 1705, and 550 cm^{-1} are observed to shift to 1422, 1200, and 400 cm^{-1}, respectively, for the perdeuterated compound. This finding appears to confirm that small amounts of impure gallane are indeed generated in the metathesis of the tetrahydridogallate with gallium(III) chloride. The corresponding Raman spectrum of the solid also includes just three significant features, namely, at 1977 (s), 700 (w), and 520 cm^{-1} (w),[9] which

Table II. IR Spectra of Digallane (400–4000 cm^{-1}) in the Vapor Phase at ca. 270 K and Isolated in Solid Ar or N_2 Matrices at ca. 20 K

vapor					digallane-h_6 trapped in an Ar matrix		digallane-h_6 trapped in an N_2 matrix		
digallane-h_6		digallane-d_6[b]							
$\tilde{\nu}$/cm^{-1}	intens[a]	$\tilde{\nu}$/cm^{-1}	intens[a]	$\tilde{\nu}_H/\tilde{\nu}_D$	$\tilde{\nu}$/cm^{-1}	intens[a]	$\tilde{\nu}$/cm^{-1}	intens[a]	assignment[a,c]
1993	m	1439	m	1.3850	2015 1996	m m } *d*	2000	m	ν_8 (b_{2u}), ν(Ga–H_t)
1976 Q	m	1421 R 1416 Q 1410 P	m	1.3955	1985 1968	s m } *d*	1985	m	ν_{16} (b_{3u}), ν(Ga–H_t)
1279 R 1273 Q 1268 P	s	923 Q	s	1.3792	1283 1278 1253 1234	s m m w } *d*	1282 1258 1243	m w w } *d*	ν_{17} (b_{3u}), ν(Ga–H_b)
1202	s	860	s	1.3977	1221 1218 1213 1208 1195	s sh m m m } *d*	1220	s	ν_{13} (b_{1u}), ν(Ga–H_b)
1046	vw	757	vw		1080	vw	1075	vw	combination[e]
760	w	555	w	1.3694	773 761	m m } *d*	770	m	ν_9 (b_{2u}), ρ(GaH_2)
700	sh				695	w			combination[e]
676 R 666 P	vs	488 R 479 P	vs	1.3878	676 666	vs s } *d*	673	vs	ν_{18} (b_{3u}), δ(GaH_2)
		439	mw		659 655 653 648	m m m m } *d*	655 647	s w } *d*	ν_{14} (b_{1u}), ρ(GaH_2)[e]

[a] s strong, m medium, w weak, v very, sh shoulder, t terminal, b bridging. [b] The IR spectrum of this sample also included a number of weak absorptions attributable to $Ga_2H_nD_{6-n}$ (n = 1, 2, ...) or impurities containing both H and D. [c] Based on a Ga_2H_6 molecule presumed to have a diborane-like structure with D_{2h} symmetry, and following the numbering scheme of ref 26. [d] Matrix splitting. [e] Tentative assignment.

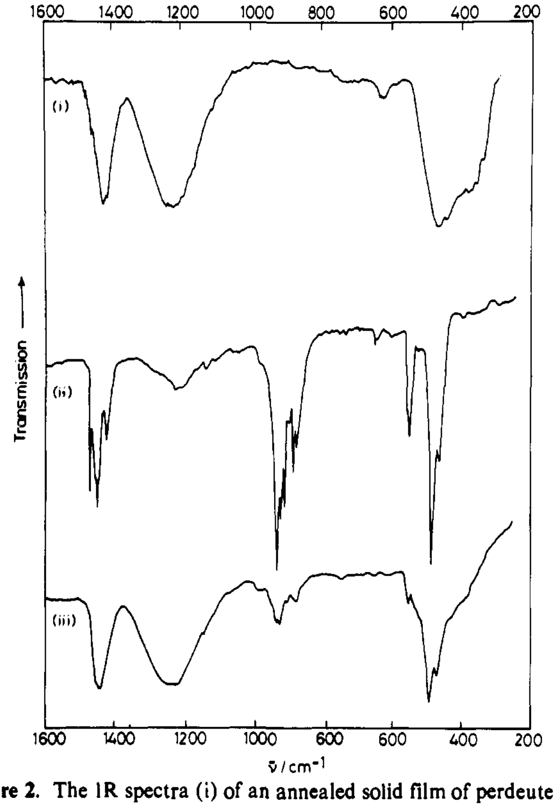
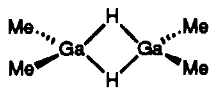


Figure 2. The IR spectra (i) of an annealed solid film of perdeuterated gallane condensed on a CsI window held at 77 K, (ii) of perdeuterated gallane vapor co-condensed with an excess of argon on a CsI window at ca. 20 K, and (iii) of the same sample as in (ii) but after annealing the matrix at temperatures up to 33 K for 15 min.

shift to 1412, 500, and 375 cm^{-1} on deuteration.

Very different IR spectra are exhibited by the vapor or by solid matrices formed by codepositing the vapor with an excess of a suitable inert gas at ca. 20 K (see Figures 2 and 3 and Table II). Here the pattern and energies of the absorptions, and particularly the rotational structure of individual absorptions of the vapor, testify to the presence of a relatively simple molecule with a momental ellipsoid in which at least one of the principal moments of inertia is unusually small for a gallium derivative. Six bands are clearly discernible in the vapor spectrum. For the isotopically natural form of the compound, these occur at 1993 (m), 1976 (m), 1273 (s), 1202 (m), 760 (w), and 671 cm^{-1} (vs),[9] and for the perdeuterated compound at 1439, 1416, 923, 860, 555, and 484 cm^{-1}. Three aspects of the spectra we judge to be critical to the unambiguous identification of the gaseous molecule.

(i) The IR spectrum of gallane vapor includes four distinct absorptions attributable to ν(Ga–H) [or ν(Ga–D)] fundamentals.[11,12,20] Of these, two occur at high energy—near 1980 (1430) cm^{-1}—in a region diagnostic of the stretching motions of terminal Ga–H bonds in a neutral gallium hydride in which the gallium center is *not* coordinated to a ligand with significant donor capacity.[10,20,21] The other two occur at substantially lower energy (1180–1300 (840–950) cm^{-1}) and are most plausibly identified with the stretching vibrations of one or more Ga–H–Ga bridges. This latter assignment receives persuasive support from the properties of dimethylgallane which, on the evidence of its mass and IR spectra and electron-diffraction pattern,[12] exists predominantly as the dimeric molecule III in the vapor at low pressures



III

and near-ambient temperatures. The IR spectrum of dimethylgallane vapor includes, in addition to the bands associated with internal motions of the Me_2Ga groups, two conspicuous features at 1290 (971) and 1185 (893) cm^{-1}, representing, re-

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(20) (a) Durig, J. R.; Chatterjee, K. K.; Li, Y. S.; Jalilian, M.; Zozulin, A. J.; Odom, J. D. *J. Chem. Phys.* **1980**, *73*, 21. (b) Baxter, P. L.; Downs, A. J.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Dalton Trans.* **1985**, 807.

(21) Greenwood, N. N. In *New Pathways in Inorganic Chemistry*; Ebsworth, E. A. V., Maddock, A. G., Sharpe, A. G., Eds.; Cambridge University Press: Cambridge, 1968; p 37.

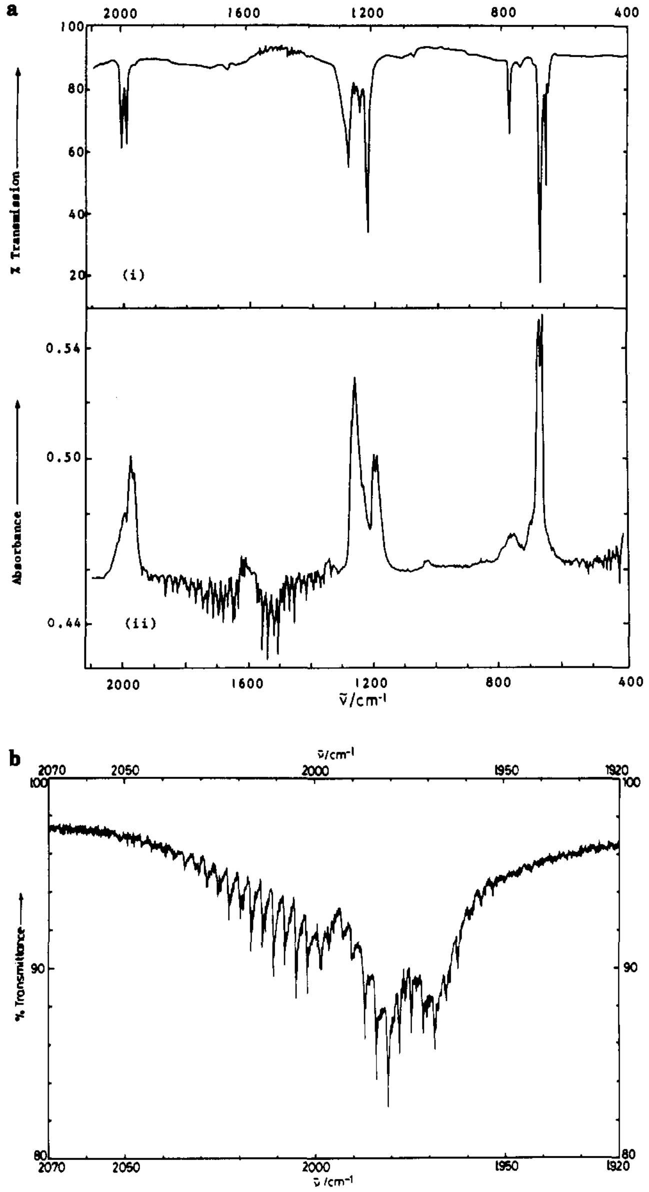
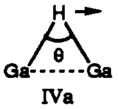
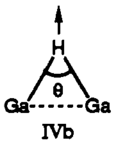


Figure 3. (a) The IR spectra of gallane vapor (i) trapped in a solid nitrogen matrix at ca. 20 K and (ii) at a pressure of ca. 5 mmHg and temperature near 270 K (contained in a cell fitted with CsI windows and having a path length of 10 cm). (b) Part of the IR spectrum of gallane vapor at a pressure of ca. 0.05 mmHg contained in a multiple-reflection cell set to a path length of 6.5 m and maintained at ca. 290 K.

spectively, antisymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations of the central Ga(μ-H)$_2$Ga moiety of III. The close resemblance which the vapor of gallane bears to that of dimethylgallane in this region of the IR spectrum invites a similar interpretation of the gallane absorptions at 1273 (923) and 1202 (860) cm^{-1}. The wavenumbers of these two vibrations, as depicted schematically for an individual Ga–H–Ga bridge in IVa and IVb,



IVa



IVb

are linked via the simple relationship 8 to the interbond angle θ,

$$\nu_{as}/\nu_s = \tan(\theta/2) \qquad (8)$$

subject, that is, to certain approximations: (a) that the mass of gallium is effectively infinite compared with that of hydrogen; (b) that the angle-bending force constant, k_θ, is much smaller than the bond-stretching force constant, k_r, and that neither ν_s nor ν_{as} experiences significant mixing with any other motion of the molecule at large; and (c) that the stretch–stretch interaction constant k_{rr} is negligible.[13b] Equation 8 requires that, as θ approaches 90°, the ratio ν_{as}/ν_s approaches unity, i.e., the separation between ν_{as} and ν_s tends to zero, and as θ approaches 180°, the ratio and frequency separation increase. There is a concomitant change in the relative intensities of the two bands, such that the ratio I_{as}/I_s runs from near unity to infinity as θ ranges from 90 to 180°. In the case of dimethylgallane, θ is estimated on the basis of eq 8 to be 95°; electron-diffraction measurements imply a value of 99.6°.[12] A similar calculation for gallane gives $\theta = 93°$, clearly arguing for a structure similar to that of III and so adducing strong circumstantial evidence that the absorber is Ga$_2$H$_6$ with a diborane-like structure II.

(ii) Most of the bands in the IR spectrum of the vapor betray the unmistakable signs of rotational structure. For example, Figure 3 illustrates the appearance of the two absorptions near 1980 cm^{-1} as measured at high resolution, with the aid of a multiple reflection cell set to a 6.5-m path; these and other features of the rovibrational spectrum of gallane are now being measured and analyzed in detail, with results to be reported elsewhere.[15] There are, it appears, two types of bands. One type, represented by the bands at 1976, 1273, and 671 cm^{-1}, displays all the features characteristic of a *parallel* band of a highly prolate symmetric top molecule, being dominated by more-or-less structured P and R branches flanking a single, very narrow Q branch. With the other type, the P and R branches form an unresolved or only partially resolved background, and any discrete structure is provided by a regular series of Q subbranches (as witness the band at 1993 cm^{-1} in Figure 3); these are the attributes of a *perpendicular* band of a symmetric top molecule. Under modest resolution, the parallel-type features assume the P–R doublet envelopes one associates with the parallel-type transitions of a linear molecule. In fact, Ga$_2$H$_6$ with structure II is quite a close approximation to such a molecule, the positioning of the two massive gallium atoms on a common symmetry axis leading to a momental ellipsoid with $I_A \ll I_B \approx I_C$. In this situation we may draw on another approximate relationship, viz. eq 9,[22] to derive a rough

$$\Delta\nu_{PR} = \sqrt{8kT\bar{B}/hc} \qquad (9)$$

estimate of the mean rotational constant $\bar{B}$, where $\bar{B} = {}^1/_2(B + C)$, k is Boltzmann's constant, T is the temperature, h is Planck's constant, and c is the velocity of light. At 10.3 ± 0.5 cm^{-1}, the average P–R branch separation, $\Delta\nu_{PR}$, of the absorptions at 1976, 1273, and 671 cm^{-1} thus implies a $\bar{B}$ value of about 0.066 ± 0.007 cm^{-1}, leading to a rough estimate of 260 ± 15 pm for the Ga···Ga distance in a molecule assumed to have the structure II (with reasonable allowance for the small contribution made to the $\bar{B}$ value by the hydrogen atoms). That this result should be so close to the corresponding distance of 261 pm in the related molecule Me$_2$Ga(μ-H)$_2$GaMe$_2$ (III), as determined by electron diffraction,[12] lends cogency to the identification of Ga$_2$H$_6$ as the principal carrier of the IR spectrum characterizing gallane in the vapor phase.

(iii) The IR spectrum of the vapor species isolated in a solid inert matrix at low temperatures resembles closely that of the vapor itself in the pattern and wavenumbers of its bands. While sharpening the absorptions and facilitating their identification in some cases, matrix isolation results typically in the development of multiplet rather than singlet absorptions, presumably as a result of the trapping of gallane molecules in different sorts of matrix cage. Such effects are particularly pronounced for argon matrices, significantly less so for nitrogen matrices. This is by no means the first time that nitrogen has proved to be spectroscopically superior to argon as a matrix material,[23] possibly because of the stronger and more specific interactions which the trapped mole-

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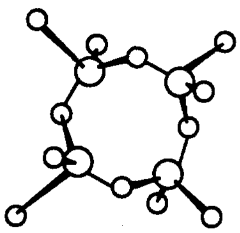
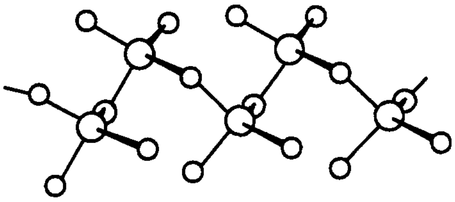
(22) Herzberg, G. *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand: Princeton, NJ, 1945; p 391.

(23) See, for example: Ogden, J. S.; Williams, S. J. *J. Chem. Soc., Dalton Trans.* **1982**, 825. Hope, E. G.; Jones, P. J.; Levason, W.; Ogden, J. S.; Tajik, M.; Turff, J. W. *Ibid.* **1985**, 529. Brisdon, A. K.; Gomme, R. A.; Ogden, J. S. *Ibid.* **1986**, 2725. Burczyk, K.; Downs, A. J. *Ibid.* **1990**, 2351.

cules experience with N_2 molecules. Most notable, however, is the finding that the IR spectrum of the matrix-isolated gallane undergoes a marked change when the deposit is annealed at temperatures up to ca. 35 K, with the appearance and growth of bands akin to those of solid gallane (notably the broad features centered near 1700 and 550 cm^{-1}) and the simultaneous decay of the bands associated with Ga_2H_6 molecules (see Figure 2). Hence it emerges that Ga_2H_6 molecules are subject to facile aggregation to give, at least in the first instance, a discrete oligomer, possibly the tetramer $[GaH_3]_4$ with a cyclic configuration such as V involving single hydrogen bridges between adjacent gallium atoms (cf. the structure of $[Me_2AlF]_4$ as determined by electron diffraction[24]). Such a structure is certainly consistent with the energies and relative intensities of the IR absorptions associated with the stretching vibrations of bridging Ga–H functions (see Table I), which imply that the Ga–H–Ga angle (θ) has now opened out to at least 120°.[13] It is also in keeping with the observation of a strong absorption near 1980 (1420) cm^{-1} signalling the retention of terminal Ga–H bonds (cf. solid α-AlH_3 which shows only a single absorption at ca. 1600 cm^{-1} correlating with the stretching of Al–H–Al bridges[25]). The physical properties of solid gallane—its volatility and solubility in solvents like toluene—favor the belief that it too consists of discrete oligomers like V, rather than an extended one-dimensional polymer along the lines of VI. Whatever form gallane may take, however, the results of the matrix experiments must surely mean that discrete Ga_2H_6 molecules exist only as transient or minority species in the condensed phases at low temperatures.



V



VI

The Ga_2H_6 molecule belongs presumably, like B_2H_6, to the D_{2h} point group, in which its 18 vibrational fundamentals span the representation $4a_g + 1a_u + 2b_{1g} + 2b_{1u} + 2b_{2g} + 3b_{2u} + 1b_{3g} + 3b_{3u}$. Eight of these fundamentals ($2b_{1u} + 3b_{2u} + 3b_{3u}$) should be active in IR absorption, two approximating to ν(Ga–H_t) modes ($b_{2u} + b_{3u}$), two to ν(Ga–H_b) modes ($b_{1u} + b_{3u}$), and the other four to deformation modes of one sort or another. By general consent, the b_{3u} modes develop dipole changes parallel to the Ga···Ga axis and should therefore give rise to type-*A* or parallel IR bands; two of these, ν_{17} and ν_{18}, are predicted to be the most intense features in the IR spectrum.[16] The b_{1u} and b_{2u} modes entail dipole changes in directions perpendicular to the Ga···Ga axis and should therefore give rise to IR bands with the characteristics of perpendicular-type transitions, but there is no common consent about which axis relates to which symmetry class. We have chosen here to follow the convention of Duncan et al. in their definitive account of the vibrational spectra of diborane,[26] thereby interchanging the labeling of the b_{1u} and b_{2u} modes referred to in our preliminary communication.[14] As a consequence of this convention, b_{1u} modes should formally give rise to type-*C* and b_{2u} modes to type-*B* IR bands, although the near-identity of the rotational constants *B* and *C* is likely to minimize the difference between the two types of contour. The IR spectrum of gallane vapor conforms, within the limits of detection and wavenumber range imposed on the present measurements, to a pattern at one with these requirements. The full interpretation of the vapor spectra of normal and perdeuterated gallane is far from straightforward,[15] but we have succeeded in analyzing the main features in terms of fundamental vibrational transitions associated with the molecules Ga_2H_6 and Ga_2D_6; the relevant assignments are given in Table II. Our reasoning has been based on six principal criteria: (i) the selection rules expected to govern the activity of modes in IR absorption; (ii) the effect of deuteration on the energy of a given spectroscopic transition; (iii) the rotational fine structure, wholly or partially resolved, associated with individual vibrational bands; (iv) analogies with the vibrational properties of related molecules, notably $[H_2GaCl]_2$,[11] $[Me_2GaH]_2$,[12] $H_2Ga(\mu\text{-}H)_2BH_2$,[15,19] $Me_3N{\cdot}GaH_3$,[20a] $[Me_2NGaH_2]_2$,[20b] and B_2H_6;[26] (v) the harmonic frequencies and IR intensities calculated for the molecules Ga_2H_6 and Ga_2D_6 on the basis of ab initio MO techniques;[16] and (vi) the results of normal coordinate analysis calculations.

On the evidence of the band contours, energies, and intensities, the IR absorptions at 1976 (1416), 1273 (923), and 671 (484) cm^{-1} must be identified, in the final analysis, with the b_{3u} fundamentals ν_{16}, ν_{17}, and ν_{18}. Such an assignment complies with the results of product-rule calculations, with the ratio $P_{obsd} = \nu_{16}(H){\cdot}\nu_{17}(H){\cdot}\nu_{18}(H)/\nu_{16}(D){\cdot}\nu_{17}(D){\cdot}\nu_{18}(D) = 2.6710$ differing from $P_{calcd} = 2.7681$ by no more than 3.5%, in accordance with the behavior normally shown by observed (anharmonic) vibration frequency data. With respect to ν_{17}, this involves a change in the assignment proposed on the basis of our preliminary assessment of the spectrum.[14] The interpretation we judge now to be correct is supported not only by the intensity and energy of the band, but also by the rotational structure which becomes discernible in the vapor spectrum under high resolution and which manifests all the characteristics of a type-*A* parallel transition. The change also brings the experimental findings into line with the results of theoretical calculations.[16] There is no mistaking the feature at 1993 (1439) cm^{-1} in the vapor spectrum for anything but a perpendicular band, and so the identification of the ν(Ga–H_t) fundamental ν_8 (b_{2u}) cannot be in doubt. Partly by elimination and partly on the evidence of its band contour, energy, and intensity, the absorption at 1202 (860) cm^{-1} is linked with the fundamental $\nu_{13}(b_{1u})$, in which ν(Ga–H_b) is the predominant motion; at higher resolution, the pronounced P–R doublet structure of the vapor band [which caused it originally to be mistaken for ν_{17} (b_{3u})] is revealed to be modified by some Q-branch structure to yield a contour consistent with its being a type-*C* perpendicular band. It has not yet been possible to examine the detailed contour of the weak-to-medium absorption at 760 (555) cm^{-1}, but the location, allied to the results of theoretical[16] and normal coordinate calculations, argues that it arises from what is mainly a GaH_2 rocking mode ν_9 (b_{2u}). The b_{1u} deformation mode ν_{14} (dominated by the GaH_2 wagging motion) is expected to occur at an energy ca. 30 cm^{-1} lower than ν_{18} (b_{3u}). No distinct absorption clearly answering to this transition has been definitely located in the IR spectrum of the vapor, although a band of medium-weak intensity at 439 cm^{-1} attributable to Ga_2D_6 is a possible candidate. The suspicion that it is obscured by the envelope of the very intense band due to ν_{18} is strengthened by the observation of significant absorption near 650 cm^{-1} in the spectrum of matrix-isolated gallane, but the picture is clouded by the potential complications of matrix site effects. Of the fundamentals active in IR absorption, that leaves only the ring-puckering mode ν_{10} (b_{2u}); this is expected to occur in the region of 200 cm^{-1} and therefore falls outside the wavenumber range of the vapor measurements described here (400–4000 cm^{-1}).

(iv) **^1H NMR Spectrum.** The ^1H NMR spectrum of gallane dissolved in toluene-d_8 at −65 °C consists of two singlets at δ 4.41

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(24) Gundersen, G.; Haugen, T.; Haaland, A. *J. Organomet. Chem.* **1973**, *54*, 77.

(25) Roszinski, H.; Dautel, R.; Zeil, W. *Z. Phys. Chem.* (*Frankfurt am Main*) **1963**, *36*, 26.

(26) Duncan, J. L.; McKean, D. C.; Torto, I.; Nivellini, G. D. *J. Mol. Spectrosc.* **1981**, *85*, 16.

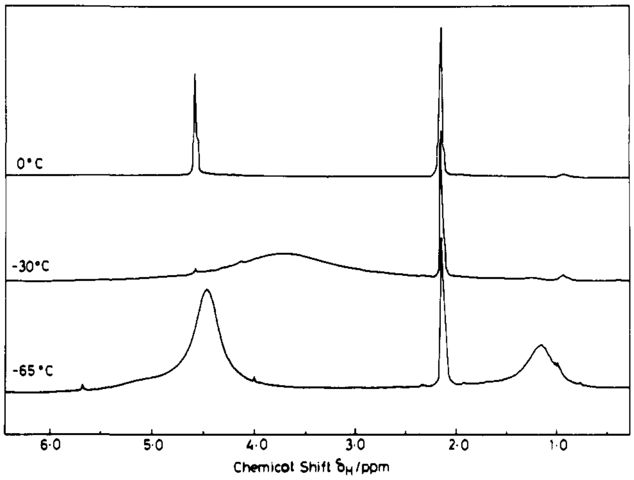

Figure 4. The ^{1}H NMR spectrum of a $C_6D_5CD_3$ solution of gallane recorded with the sample held successively at −65, −30, and 0 °C. The resonance near δ_H 2.1 is due to residual C_7D_7H in the solvent.

and 1.11 with relative intensities in the ratio 2:1 (see Figure 4), both showing the broadness characteristic of protons directly bound to gallium atoms.[21] It is tempting to correlate this finding with the presence of Ga_2H_6 molecules having the structure II, a conclusion sustained by the relative volatility of the gallane under these conditions. However, the ready aggregation of Ga_2H_6 revealed by the matrix experiments must leave such an interpretation open to serious doubt. In fact, the spectrum does not differentiate between Ga_2H_6 and any other oligomer like V containing terminal and bridging hydrogen atoms in the proportions 2:1.[27] Warming the sample to −30 °C results in broadening and coalescence of the two resonances, indicating rapid exchange between bridging and terminal proton sites. The single broad resonance displayed by the sample at −30 °C occurs at δ 3.7, a chemical shift appreciably different from the weighted mean (δ 3.31) of the shifts characterizing the separate resonances observed at lower temperatures. It seems therefore that more than one molecule is implicated in the exchange process. Further warming to 0 °C results in decomposition of the sample, with the production of a gray suspension of gallium metal accompanying the disappearance of the broad Ga–H resonance and the growth of a new sharp signal at δ 4.5 attributable to dihydrogen.[28] Once started, the decomposition is rapid, and we have failed so far to detect any sign of gallium hydride intermediates formed en route to elemental gallium and hydrogen. However, the possibilities that polygallane intermediates like Ga_4H_{10} may be formed (cf. the decomposition of diborane[2]) and that they may be amenable to physical or chemical trapping are still being actively explored.

(v) Structure of Gaseous Digallane As Determined by Electron Diffraction. Using a specially constructed all-glass inlet system maintained at a temperature between −15 and −20 °C, we have succeeded in measuring the electron-diffraction pattern of gallane vapor. The measurements have been carried out at two camera distances, viz. ca. 200 and 260 mm at an electron wavelength of 5.671 pm to give results spanning the range 20–212 nm^{-1} in the scattering variable s. Similar studies of other volatile gallium hydrides[11,12,19,20b,29–31] or tetrahydridoborate[32,33] derivatives have prepared us for the technical problems of sampling highly reactive and thermally fragile molecules, but none has proved more challenging than gallane itself. Chief among the obstacles to success is the propensity of the strongly reducing vapor to react with the emulsion of the photographic plates; the resulting fogging effects can be minimized, but not eliminated, by leaving the washed plates exposed to air for about 24 h prior to developing.

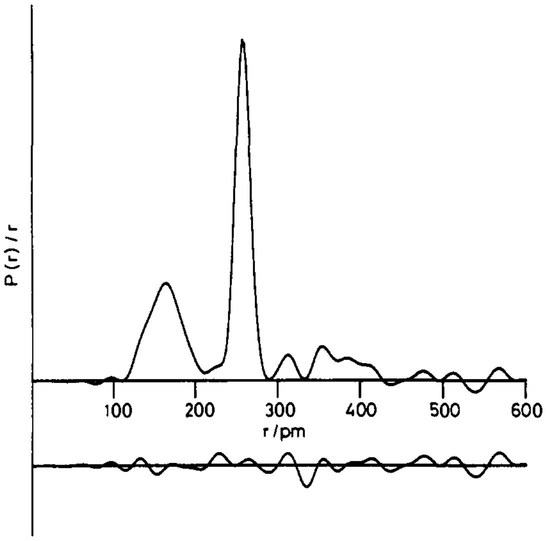

Figure 5. Observed and difference radial-distribution curves, $P(r)/r$ against r, for digallane vapor; before Fourier inversion, the data were multiplied by $s\ \exp[(-0.000020s^2)/(Z_{Ga} - f_{Ga})^2]$.

Our reading of the IR spectrum is that the vapor consists mainly, if not exclusively, of Ga_2H_6 molecules with the structure II. Accordingly, this is the model we have adopted as a basis for calculating the molecular scattering of the vapor species. The model has been specified in terms of four independent geometrical parameters. These comprise the distance $r(Ga\cdots Ga)$, a *mean* Ga–H distance, $r(Ga-H)_{mean}$, the difference $\Delta r(Ga-H)$ between the $Ga-H_b$ and $Ga-H_t$ distances, and the bond angle $\angle H_t-Ga-H_t$. The IR spectrum gives no hint of any departure from a regular D_{2h} structure; although it would have been desirable to check the scattering pattern for any suggestion that the central $Ga(\mu-H)_2Ga$ fragment is other than planar and orthogonal to the two terminal GaH_2 units, themselves mutually coplanar, this level of refinement could not be justified by the results whose quality inevitably reflected the severe technical problems which the studies posed. Within the limits of experimental uncertainty, however, the simple model is found satisfactorily to account for the radial-distribution curve deduced from the measured scattering pattern of gallane vapor (see Figure 5).

The experimental radial-distribution curve, which bears an obvious kinship to that of B_2H_6,[34] is distinguished by just two prominent peaks. Occurring near 160 and 260 pm, these plainly correspond to scattering from Ga–H and Ga⋯Ga atom pairs, respectively. The only other significant feature clearly in evidence is a weak peak near 350 pm which correlates with scattering from nonbonded Ga⋯H atom pairs. That long-range atom pairs do not make a greater contribution to the scattering tends to confirm that Ga_2H_6 is the predominant vapor species under the conditions of the experiments, since higher oligomers like $[GaH_3]_4$ (V) would surely contain Ga⋯Ga atom pairs with separations exceeding 300 pm.

Molecular-scattering intensities have been calculated, and the molecular structure has been refined on the basis of the model described above by full-matrix least-squares analysis.[35] For the

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[27] If $[GaH_3]_4$ has a *rigid* structure V directly analogous to that of $[Me_2AlF]_4$ (see ref 24), then the ^{1}H NMR spectrum may be expected to show an AB pattern corresponding to the distinct exo and endo locations of the hydrogen atoms in the terminal GaH_2 units. That such a pattern is not observed may be a function of the broadness of the resonance, or it may mean that the molecule is open to facile exchange.

[28] Dayan, E.; Widenlocher, G.; Chaigneau, M. *C. R. Acad. Sci. Paris* **1963**, *257*, 2455.

[29] Baxter, P. L.; Downs, A. J.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* **1984**, 1755.

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[31] Pulham, C. R.; Downs, A. J.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Chem. Commun.* **1990**, 1520.

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[33] Dain, C. J.; Downs, A. J.; Rankin, D. W. H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 534. Dain, C. J.; Downs, A. J.; Goode, M. J.; Evans, D. G.; Nicholls, K. T.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Dalton Trans.* **1991**, 967.

[34] Bartell, L. S.; Carroll, B. L. *J. Chem. Phys.* **1965**, *42*, 1135.

Table III. Least-Squares Correlation Matrix (×100) for the Analysis of the Electron-Diffraction Pattern of Ga_2H_6

r(Ga···Ga)	$r(\text{Ga–H})_{\text{mean}}$	Δr(Ga–H)	u(Ga···Ga)	$u(\text{Ga–H}_b)$	$u(\text{Ga···H}_t)$	$k_1{}^a$	$k_2{}^a$	
100	−2	26	−5	−25	−7	−8	−6	r(Ga···Ga)
	100	22	4	−14	0	9	3	$r(\text{Ga–H})_{\text{mean}}$
		100	−33	−96	−3	−39	−33	Δr(Ga–H)
			100	42	9	73	76	u(Ga···Ga)
				100	5	49	42	$u(\text{Ga–H}_b)$
					100	11	15	$u(\text{Ga···H}_t)$
						100	59	$k_1{}^a$
							100	$k_2{}^a$

[a] Scale factor.

Table IV. Molecular Parameters Deduced from the Electron-Diffraction Pattern of Ga_2H_6[a] and Compared with the Results of ab Initio Calculations[b]

	distance (pm) or angle (deg)		
parameter	experimental[c]	ab initio calculations TZP SCF basis set[b]	vibrational amplitude[c] (pm)
	(a) Independent Parameters[d]		
r(Ga···Ga)	258.0 (0.2)	264.8	6.5 (0.4)
$r(\text{Ga–H})_{\text{mean}}$	161.5 (0.8)	166.5	
Δr(Ga–H)	19.1 (7.1)	21.3	
$\angle H_t\text{–Ga–}H_t$	130[e]	129.1	
	(b) Dependent Parameters[d]		
$r(\text{Ga–H}_t)$	151.9 (3.5)	155.8	10.0[f]
$r(\text{Ga–H}_b)$	171.0 (3.8)	177.1	12.0 (5.1)
$r(\text{Ga···H}_t)$	350.4 (2.5)	360.4	32.9 (8.2)
$r(\text{H}_b\text{···H}_b)$	224.6 (11.6)	235.2	14.0[e]
$r(\text{H}_b\text{···H}_t)$	262.5 (1.1)	270.9	14.0[e]
$r(\text{H}_t\text{···H}_t)$	275.3 (6.3)	281.4	14.0[e]
$r(\text{H}_t\text{···H}_t')_{\text{cis}}$	386.4 (2.9)	398.7	20.0[e]
$r(\text{H}_t\text{···H}_t')_{\text{trans}}$	474.4 (6.0)	488.0	25.0[e]
$\angle \text{Ga–H}_b\text{–Ga}$	97.9 (3.2)	96.8	

[a] Figures in parentheses are the estimated standard deviations of the last digits. [b] Reference 16a. [c] This work. [d] H_b bridging H atom, H_t terminal H atom, H_t' atom attached to *different* Ga atom, $\Delta r(\text{Ga–H}) = r(\text{Ga–H}_b) - r(\text{Ga–H}_t)$. [e] Fixed. [f] Tied to $u(\text{Ga–H}_b)$ (see text).

present, we have been content to determine the r_a structure without reference to possible "shrinkage" corrections,[36] although there is no reason to suppose that such corrections would alter the principal results of our structure analysis. Following a detailed analysis of the rovibrational spectra of different isotopomers of gallane, we aim to combine the results with those of the electron-diffraction experiments to secure a more complete and precise definition of the molecular structure.[15,36,37] The two independent distances r(Ga···Ga) and $r(\text{Ga–H})_{\text{mean}}$ and the split Δr(Ga–H) used to specify the Ga_2H_6 model are found to refine in a straightforward manner. Although the H_t-Ga-H_t angle is specified by the dimensions of the GaGaH_t triangle, all three sides of which correlate with discernible scattering, two of the sides [$r(\text{Ga–H}_t)$ and $r(\text{Ga···H}_t)$] are subject to large uncertainties, and the angle is correspondingly ill-determined; it has therefore been fixed at 130°. Such a value is in line not only with the predictions of theoretical calculations,[16] but also with preliminary estimates of the difference between the rotational constants $A - \bar{B}$ derived from a detailed analysis of the IR band due to the $\nu(\text{Ga–H}_t)$ fundamental ν_8.[15] Independent refinement has been accomplished too for just three amplitudes of vibration, viz., those associated with the Ga···Ga, $\text{Ga–H}_b/\text{Ga–H}_t$, and Ga···H_t vectors [u(Ga–H) being refined as a single parameter with the ratio $u(\text{Ga–H}_b)/u(\text{Ga–H}_t)$ constrained to a value of 1.2:1 consistent with the appropriate distances]. Otherwise, we have drawn on the precedents set by related molecules, e.g., $H_2Ga(\mu\text{-Cl})_2GaH_2$[11] and $H_2Ga(\mu\text{-H})_2BH_2$,[19] to arrive at reasonable values for the remaining amplitudes which make only minor contributions to the overall molecular scattering.

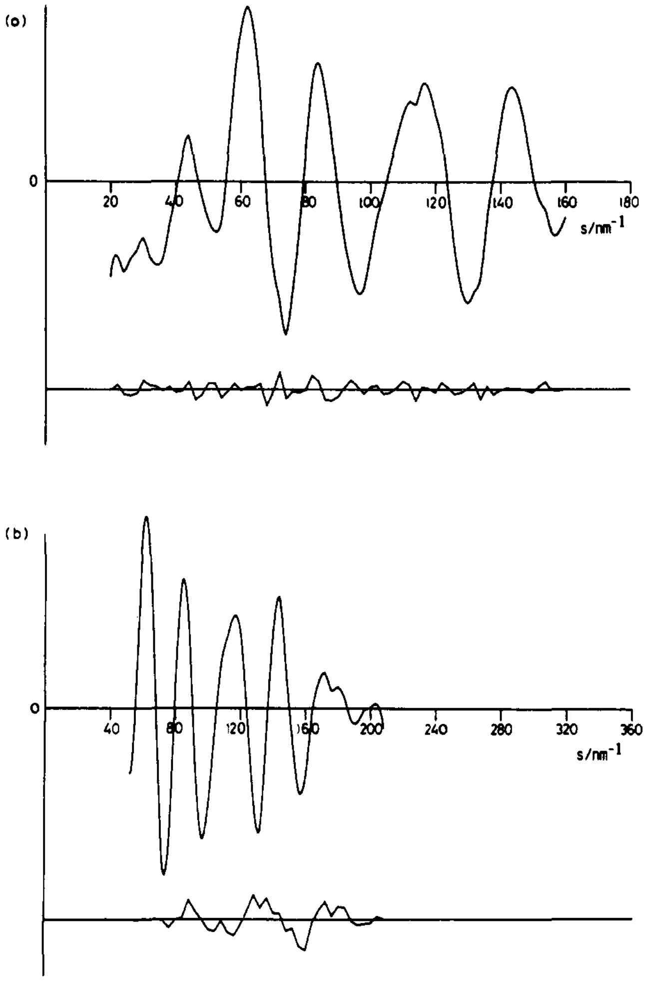

Figure 6. Experimental and final difference molecular-scattering intensities for digallane; nozzle-to-plate distances (i) 259.80 and (ii) 201.22 mm.

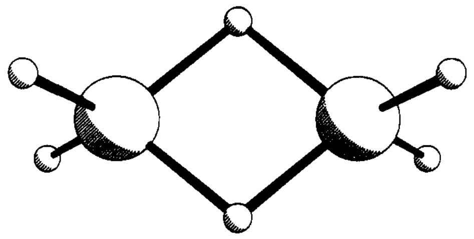

Figure 7. Perspective view of the digallane molecule in the optimum refinement of the electron-diffraction measurements.

The success of the analysis may be gauged from the difference between the experimental and calculated radial-distribution curves (Figure 5). Figure 6 offers a similar comparison between the experimental and simulated molecular scattering. As revealed by the uncertainties in the quoted results and the elements of the

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Table V. A Comparison of the Dimensions of Ga_2H_6 with Those of Some Related Hydride Molecules

molecule	heavy atoms M, M′	r(M···M′) (pm)	r(M–H_t) (pm)	r(M–H_b) (pm)	∠M–H_b–M′ (deg)	ref
B_2H_6	M = M′ = B	177.5 (0.4)	119.6 (0.8)	133.9 (0.6)	83.0 (0.3)	33
$Me_2B(\mu\text{-}H)_2BMe_2$	M = M′ = B	184.0 (1.0)		136.4 (4.5)	85 (5)	*a*
Ga_2H_6	M = M′ = Ga	258.0 (0.2)	151.9 (3.5)	171.0 (3.8)	97.9 (3.2)	this work
$Me_2Ga(\mu\text{-}H)_2GaMe_2$	M = M′ = Ga	261.0 (0.5)		170.8 (1.4)	99.6 (1.4)	12
$H_2Ga(\mu\text{-}Cl)_2GaH_2$	M = M′ = Ga	324.1 (0.7)	155.9 (1.9)			11
$H_2Ga(\mu\text{-}H)_2BH_2$	M = Ga, M′ = B	217.9 (0.2)	158.6 (0.8)	182.6 (0.8)	85.7 (2.0)	19
$Me_2Ga(\mu\text{-}H)_2BH_2$	M = Ga, M′ = B	216.3 (0.8)		179.1 (3.0)	89.9 (4.2)	31

[a] Carroll, B. L.; Bartell, L. S. *Inorg. Chem.* **1968**, *7*, 219.

final least-squares correlation matrix reproduced in Table III, the main problem confronting refinement is the similarity of the Ga–H_b and Ga–H_t distances, causing the split Δr(Ga–H) to be very strongly correlated with the amplitudes of vibration for the Ga–H vectors. This correlation is the main author of the large uncertainties affecting the individual Ga–H bond lengths. The optimum refinement, corresponding to $R_G = 0.15$ ($R_D = 0.14$), affords the structure illustrated in Figure 7, with the dimensions and vibrational amplitudes listed in Table IV. The estimated standard deviations allow for the effects of correlation and take account also of systematic errors in the electron wavelength, nozzle-to-plate distances, etc.

When compared with related hydride molecules of the group III (13) elements (see Table V), Ga_2H_6 holds comparatively few structural surprises. There are just three aspects which catch the eye.

(a) r(Ga···Ga). At 258.0 pm, the measured Ga···Ga distance in Ga_2H_6 is pleasingly close to the first rough estimate gained from the parallel band envelopes in the IR spectrum.[14] Equally reassuring is its proximity to the corresponding distance of 261.0 pm in the molecule $Me_2Ga(\mu\text{-}H)_2GaMe_2$.[12] This parameter is to be compared, not only with twice the covalent radius of tetrahedrally coordinated gallium (252 pm),[38] but also with the Ga–Ga distances ranging from 247 to 307 pm in the different forms of elemental gallium.[39] Combined with the relatively small amplitude of vibration of the Ga···Ga vector, the short Ga···Ga distance in Ga_2H_6 makes a persuasive case for direct interaction between the two metal atoms, notwithstanding theoretical contentions that no such bond path exists.[16b]

(b) r(Ga–H). Despite the large uncertainties, originating mainly in the problems of correlation noted above, the refined amplitudes of vibration for the Ga–H bonds assume reasonable values.[11,12,19,29,30] It is likely, then, that the difference between the bridging and terminal Ga–H bond lengths, which is also less than well defined, is no less reasonable. At about 20 pm, this difference is to be compared with 14.3 and 20.1 pm for the corresponding parameters in the molecules B_2H_6[34] and Ga_2Cl_6,[40] respectively. The Ga–H_b bonds in Ga_2H_6 are effectively identical in length with those in $Me_2Ga(\mu\text{-}H)_2GaMe_2$[12] (171.0 versus 170.8 pm), while being appreciably longer than the Ga–H_t bonds, themselves comparable in extent (151.9 pm) with similar bonds in molecules like $Me_3N{\cdot}GaH_3$ (149.7 pm),[29] $[Me_2NGaH_2]_2$ (148.7 pm),[20b] $HGa(BH_4)_2$ (156.5 pm),[30] $H_2Ga(\mu\text{-}H)_2BH_2$ (158.6 pm),[19] and $[H_2GaCl]_2$ (155.9 pm).[11] This is in keeping with the normal sacrificial behavior shown by a metal-hydrogen bond on coordination to a second metal atom; it correlates too with the substantially smaller stretching force constants of the bridging compared with the terminal Ga–H bonds (q.v.). On the other hand, the Ga–H_b bond in Ga_2H_6 is somewhat shorter than those in the molecules $H_2Ga(\mu\text{-}H)_2BH_2$ (182.6 pm)[19] and $Me_2Ga(\mu\text{-}H)_2BH_2$ (179 pm)[32] containing unsymmetrical Ga–H–B bridges in which there is presumably a greater charge separation between the gallium and hydrogen centers.

(c). Table IV also includes the dimensions calculated in one of several recent ab initio studies of the molecule Ga_2H_6 carried out at the SCF level using basis sets of slightly less than triple-zeta plus polarization (TZP) quality.[16a] There is tolerably good agreement between these and the experimental parameters, although the Ga···Ga and Ga–H distances are estimated to be 4–7 pm longer than the values we find. Irrespective of the precise basis set adopted, all the ab initio calculations reported so far[16] seem to point to a value near 130° for the H_t–Ga–H_t angle, which could not be determined meaningfully from the electron-diffraction pattern. According to other theoretical calculations involving the molecules $H_2Ga(\mu\text{-}H)_2BH_2$[41a] and $[H_2GaCl]_2$,[41b] such a value seems to be endemic to the $H_2Ga(\mu\text{-}X)_2$ moiety (X = H or Cl).

(vi) Chemical Properties of Gallane. Some of the chemical properties of gallane have been explored, with the results summarized in Scheme I. Reference has already been made to the decomposition to the elements at ambient temperatures and also to the quantitative reaction with anhydrous hydrogen chloride at −95 °C (eq 7). Our preliminary survey of the chemistry of gallane has, in addition, taken in its behavior with respect to each of three selected Lewis bases (NMe_3, NH_3, and PH_3) and to a representative unsaturated organic molecule (C_2H_4). Each of these four reactions will now be treated in turn.

(a) Reaction with NMe_3. One of the earliest experiments to be undertaken with gallane established that it reacts with an excess of trimethylamine at −95 °C. There is but a single product, a white solid identifiable by its spectroscopic properties as the molecular adduct $(Me_3N)_2GaH_3$,[42] which survives more-or-less intact in the condensed phases at low-to-ambient temperatures. Thus, the ^1H NMR spectrum of a benzene-d_6 solution shows two singlets, one broad at δ 5.0 and the other sharp at δ 1.92 attributable to the protons of the GaH_3 and NMe_3 moieties, respectively (cf. the adduct $Me_3N{\cdot}GaH_3$ for which the corresponding chemical shifts are δ 4.46 and 2.01[43]). Vaporization of the solid proceeds with dissociation to the 1:1 adduct $Me_3N{\cdot}GaH_3$ and free trimethylamine.[42] Thus, the IR and Raman spectra of the solid condensate formed by quenching the vapor at −196 °C testify to the presence of *both* $Me_3N{\cdot}GaH_3$ and $(Me_3N)_2GaH_3$ (regenerated presumably on condensation of the 1:1 adduct and free trimethylamine). The vibrational spectra of our condensate can be explained (see Table VI) with reference to the well-established vibrational properties of $Me_3N{\cdot}GaH_3$[20a] and to the properties anticipated for $(Me_3N)_2GaH_3$ in which the N_2GaH_3 skeleton is assumed to take the form of a trigonal bipyramid with the nitrogen atoms in the apical and the hydrogen atoms in the equatorial sites. The partially determined crystal structure of the corresponding alane $(Me_3N)_2AlH_3$ implies a similar structure,[44a] and the vibrational spectra reported for this compound,[44b] which show a close affinity to those associated with $(Me_3N)_2GaH_3$, provide obvious guidelines to the present analysis. Despite some discrepancies between the assignments proposed previously (based exclusively on IR measurements)[42] and those listed in Table VI, all the main features of the spectra can be satisfactorily interpreted, with only

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Scheme I. Preparation and Some Reactions of Gallane

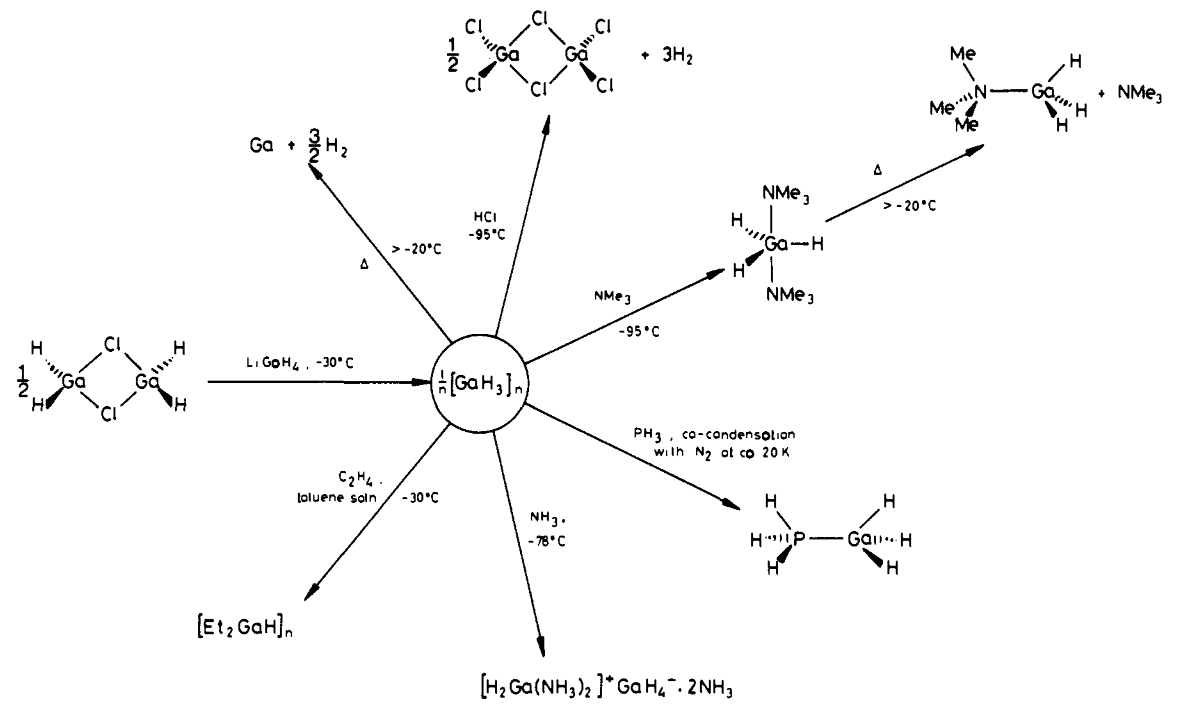

Table VI. Vibrational Spectra (400–2000 cm^{-1}) of an Annealed Solid Film of the Condensate Formed at 77 K by Vaporizing the Solid Product of the Reaction between Gallane and Trimethylamine

IR spectrum		Raman spectrum			
$\tilde{\nu}$/cm^{-1}	intens[a]	$\tilde{\nu}$/cm^{-1}	intens[a]	species[b]	assignment[c]
		1861	vs	1:1	sym ν(Ga–H) (a_1)[d]
1839	vs, br	1850	w, sh	1:1	antisym ν(Ga–H) (e)[d]
		1797	vs	2:1	sym ν(Ga–H) (a_1')
1790	sh	1790	sh	2:1	antisym ν(Ga–H) (e′)
1480	s, sh				
1467	vs	1454	m	1:1 + 2:1	antisym $\delta(CH_3)$[d]
1448	s, sh	1435	m		
1404	m	1402	w	1:1 + 2:1	sym $\delta(CH_3)$[d]
1270	m	1271	vw	free Me_3N	$\rho(CH_3)$ + antisym ν(C–N)[d]
1253	m	1252	vw	1:1	$p(CH_3)$ + antisym ν(C–N) (e)[d]
1233	m	1226	w		
1209	w	1210	w	2:1	$\rho(CH_3)$ + antisym ν(C–N)
1186	vw			free Me_3N	$\rho(CH_3)$[d]
		1122	w	2:1	$\rho(CH_3)$
1103	m	1104	vw	1:1	$\rho(CH_3)$ (e)[d]
1038	m			free Me_3N	antisym ν(C–N) + $\rho(CH_3)$[d]
1024	m	1028	w	2:1	antisym ν(C–N) + $\rho(CH_3)$
1004	vs	1000	s	1:1	antisym ν(C–N) + $\rho(CH_3)$ (e)[d]
846	w	833	m	2:1	sym ν(C–N)
829	w	825	m	1:1	sym ν(C–N) (a_1)[d]
780	sh			2:1	out-of-plane $\delta(GaH_3)$ (a_2'')
		762	sh	2:1	in-plane $\delta(GaH_3)$ (e′)
747	vs, br	750	m	1:1	antisym $\delta(GaH_3)$ (e)[d]
		716	m	1:1	sym $\delta(GaH_3)$ (a_1)[d]
677	m			2:1	overtone or combination?
		596	m	2:1	$\rho(GaH_3N_2)$ (e″)
530	s	536	sh	1:1	$\rho(GaH_3)$ (e)[d]
		524	m		
504	s	504	m	1:1	ν(Ga–N) + sym $\delta(NC_3)$ (a_1)[d]
440	w			2:1	antisym ν(Ga–N) (a_2'')
422	m	416	m	1:1	antisym $\delta(NC_3)$ (e)[d]
		405	sh	2:1	sym ν(Ga–N) (a_1')

[a] s strong, m medium, w weak, v very, br broad, sh shoulder. [b] 1:1 = $Me_3N{\cdot}GaH_3$, 2:1 = $(Me_3N)_2GaH_3$. [c] Assignments for $Me_3N{\cdot}GaH_3$ based on a molecular model in which the C_3NGaH_3 skeleton has C_{3v} symmetry; assignments for $(Me_3N)_2GaH_3$ based on a molecular model in which the N_2GaH_3 skeleton has D_{3h} symmetry. Descriptions of modes refer to the *principal* component or components of each motion. [d] See ref 20a.

the skeletal N–Ga–N bending mode of $(Me_3N)_2GaH_3$ and the torsional modes of both adducts escaping detection, presumably because they fall outside the wavenumber limits of our measurements (<400 cm^{-1}). At no stage in the reaction is elemental hydrogen released, and there is no hint of any component other than the adducts $Me_3N{\cdot}GaH_3$ and $(Me_3N)_2GaH_3$ and the free base Me_3N. The chemical trapping of gallane in this way thus affords irresistible proof of its identity.

(b) Reaction with NH_3. With an excess of ammonia at −78 °C, gallane reacts to give a white solid. Evaporation of the excess of ammonia leaves an involatile white residue which is long-lived at room temperature. At no stage is dihydrogen evolved. Ma-

Table VII. IR Spectrum (400–4000 cm^{-1}) of the Matrix Formed by Co-condensation of Gallane and Phosphine Vapors with an Excess of N_2 at ca. 20 K

IR spectrum of matrix				$\tilde{\nu}/cm^{-1}$ for corresponding mode in related molecules		
$\tilde{\nu}/cm^{-1}$	intens[a]	absorber	assignment[b]	$H_3P{\cdot}BH_3$[c]	$Me_3P{\cdot}GaH_3$[d]	H_3SiGeH_3[e]
2346	vw, br	$H_3P{\cdot}GaH_3 + PH_3$[f]	sym and antisym ν(P–H) (a_1 + e)	2394, 2425		2163.1, 2164.6
2314	s	$[PH_3]_n$[f]	ν(P–H)			
2312	s	$[PH_3]_n$[f]	ν(P–H)			
2201	vw	$H_3P{\cdot}GaH_3$	2 × 1099			
1854	mw, br	$H_3P{\cdot}GaH_3$	sym and antisym ν(Ga–H) (a_1 + e)		1808, 1832	2076.2, 2076.6
1099	m	$H_3P{\cdot}GaH_3$	antisym $\delta(PH_3)$ (e)	1101		940.5
984	m	$H_3P{\cdot}GaH_3$	sym $\delta(PH_3)$ (a_1)	992		890.3
737	mw	$H_3P{\cdot}GaH_3$	antisym $\delta(GaH_3)$ (e)		765	885.5
685	mw	$H_3P{\cdot}GaH_3$	sym $\delta(GaH_3)$ (a_1)		690	785.2
542	vw	$H_3P{\cdot}GaH_3$	$\rho(GaH_3)$ (e)		498	374.4

[a] s strong, m medium, w weak, v very, br broad. [b] Assignments for $H_3P{\cdot}GaH_3$ based on a molecular model assumed to have C_{3v} symmetry. [c] See ref 50. [d] See ref 48. [e] See ref 49. [f] See ref 47.

nometric and chemical analysis of the reaction mixture reveals that the reacting proportions Ga:NH_3 are approximately 1:2. The IR spectrum of the solid shows the absorptions characteristic of the anion GaH_4^- (notably a broad feature centered at 1809 cm^{-1}[45]) and of a cation of the type $[H_2Ga(NH_3)_x]^+$ (notably features at 3280, 3200, 1941, 1597, 1237, 780, and 523 cm^{-1} which find obvious parallels in the spectra of $[H_2Ga(NH_3)_2]^+Cl^-$[11] and Me_2GeH_2[46]). Hence it seems that gallane formally suffers unsymmetrical cleavage of the Ga–H–Ga bridges in accordance with eq 10 (cf. the behavior of diborane in similar circumstances[2]),

$$(2/n)[GaH_3]_n + 4NH_3 \rightarrow [H_2Ga(NH_3)_4]^+GaH_4^- \quad (10)$$

although we cannot be certain, on the evidence available at present, that the NH_3 molecules are coordinated exclusively to a cationic center.

(c) **Reaction with PH_3.** Gallane reacts with an excess of phosphine at −95 °C. Evaporation of the surplus phosphine gives a white solid which melts at ca. −50 °C to give a colorless viscous liquid. Attempts to vaporize the material at −30 °C result only in fragmentation with the production of phosphine, dihydrogen, and a black residue. The reacting proportions Ga:PH_3 vary from experiment to experiment (in the range 1:0.8 to 1:1.7), and so the liquid is presumed to be a mixture of compounds.

Experiments designed to monitor the interaction of gallane with phosphine in toluene-d_8 solution at low temperatures were frustrated partly by the disparate volatilities of the reagents, partly by the weakness of their interaction. The only obvious inference which could be drawn was that phosphine catalyzes the exchange of bridging and terminal hydrogen atoms in the gallane oligomer(s), $[GaH_3]_n$, to the extent that the fast-exchange regime is attained at a significantly lower temperature (−70 °C).

In a final effort to counter these problems, gallane was co-condensed with an excess of nitrogen doped with phosphine (N_2:PH_3 = ca. 20:1). The IR spectrum of the resulting condensate formed at ca. 20 K is illustrated in Figure 8, and the details, including tentative assignments, are itemized in Table VII. The results are noteworthy on several counts. Firstly, the spectrum includes *no bands* attributable to free gallane, whether as Ga_2H_6 or as a higher oligomer like V; indeed, there is no suggestion of an absorption diagnostic of a Ga–H–Ga bridge. What the spectrum does show, in addition to absorptions associated with unchanged PH_3 monomers or multimers,[47] is a relatively simple pattern of bands originating in a common source. That this source is the molecular adduct $H_3P{\cdot}GaH_3$ is argued by the resemblance the spectrum bears to those of known GaH_3 and PH_3 adducts. Thus, the absorptions at 1854, 737, and 685 cm^{-1} are more-or-less characteristic of a coordinated GaH_3 group,[20a,21] with the ν(Ga–H) modes, at 1854 cm^{-1}, significantly lower in energy than the corresponding modes of the parent gallane (ca. 1980 cm^{-1}). A satisfactory interpretation of the spectrum follows from the assumptions that $H_3P{\cdot}GaH_3$ has C_{3v} symmetry and that its vibrational properties emulate those of related molecules, e.g., $Me_3P{\cdot}GaH_3$,[48] $Me_3N{\cdot}GaH_3$,[20a] H_3SiGeH_3,[49] $H_3P{\cdot}BH_3$,[50] and other PH_3 complexes,[47,51] although certain modes [that approximating to ν(Ga–P), for example] are presumably too weak in IR absorption or too low in energy to be detected in any of the experiments carried out so far. The matrix sample is not affected either by broad-band UV irradiation or by annealing at temperatures up to ca. 30 K.

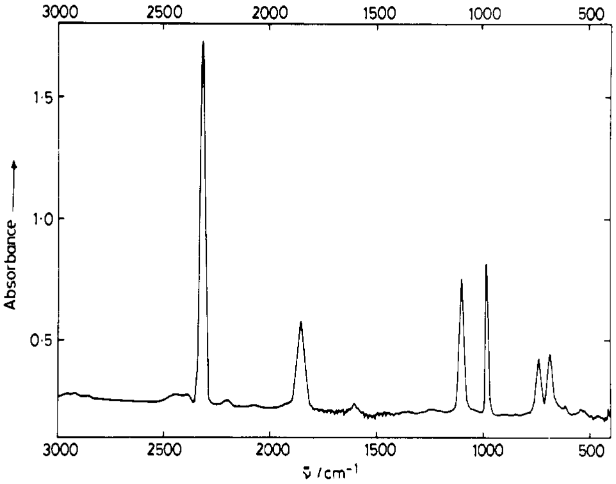

Figure 8. The IR spectrum of the matrix formed at ca. 20 K by the co-condensation of gallane with an excess of nitrogen doped with phosphine (N_2:PH_3 = ca. 20:1).

It is clear that further experiments are needed to confirm the identity of this product and to characterize its physical properties. Future plans include (i) repeating the matrix experiments with deuterated samples of one or both reagents and (ii) investigating whether the procedures employed to measure the high-resolution IR spectrum of gaseous Ga_2H_6 molecules lend themselves to the normal and deuterated versions of $H_3P{\cdot}GaH_3$. A search will also be mounted for the arsine adduct $H_3As{\cdot}GaH_3$, the stable existence of which receives support from the recent matrix isolation of the adduct $H_3As{\cdot}GaMe_3$,[52a] as well as from ab initio MO methods

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Table VIII. IR Spectra (400–4000 cm^{-1}) of Diethylgallane (i) Isolated in an N_2 Matrix at ca. 20 K and (ii) as an Annealed Solid Film at ca. 77 K

N_2 matrix			solid film		
$\tilde{\nu}$/cm^{-1}	intens[a]	effect of annealing[b]	$\tilde{\nu}$/cm^{-1}	intens[a]	assignment[c]
2951	s		2944	s	ν(C–H)
2908	s		2902	s	
2874	s		2867	s	
2818	w		2813	w	2 × $\delta(CH_3)$ or 2 × $\delta(CH_2)$
2736	vw		2730	vw	
1933	vw				$\nu(Ga–H_t)$ of Et_2GaH, $[EtGaH_2]_2$, or $Et_2GaH{\cdot}OH_2$
1647	w, br	↑	1657	s, br	$\nu(Ga–H_b)$ of $[Et_2GaH]_n$ (n = 3 or 4)
1600	w	↑			
1459	m		1462	m	antisym $\delta(CH_3)$
1421	mw		1417	w	$\delta(CH_2)$
1380	sh		1375	w	sym $\delta(CH_3)$
1375	m				
1234	s, br	↓			antisym $\nu(Ga–H_b)$ of $[Et_2GaH]_2$
			1231	sh	CH_2 wagging
			1191	m	
1162	s	↓			sym $\nu(Ga–H_b)$ of $[Et_2GaH]_2$
			1126	w	$\rho(CH_3)$
			1101	sh	
1008	ms		999	m	$\rho(CH_3)$
962	m		961	m	ν(C–C)
940	m		938	m	
749	sh				$\delta(Ga–H_t)$ of Et_2GaH, $[EtGaH_2]_2$, or $Et_2GaH{\cdot}OH_2$
722	m				
			698	sh	$\rho(CH_2)$
661	m		663	m	
571	m		563	mw	antisym ν(Ga–C)
513	m		513	mw	sym ν(Ga–C)

[a] s strong, m medium, w weak, v very, br broad, sh shoulder. [b] ↑, grows on annealing; ↓, decays on annealing. [c] Proposed assignments are based on analogies with the IR spectra of $[Et_2GaF]_3$,[53] $[Et_2GaCl]_2$,[53] EtBr (Gaufrès, R.; Bějaud-Bianchi, M. *Spectrochim. Acta*, *Part A* **1971**, *27A*, 2249), and $[Me_2GaH]_n$;[12] some of the details are necessarily tentative.

which suggest that $H_3As{\cdot}GaH_3$, with a predicted binding energy of 67 kJ mol^{-1}, should be observable in the gas phase.[52b]

(d) Reaction with C_2H_4. Ethene, at an overpressure of ca. 3 atm and in excess, reacts with a toluene solution of gallane at −30 °C. Evaporation and fractionation of the volatile material under continuous pumping yield, in addition to toluene and unchanged ethene, a fraction identifiable as diethylgallane, $[Et_2GaH]_n$. This collects as a viscous liquid in a trap held at 0 °C. The IR spectrum has been recorded with reference (a) to an annealed solid film of the condensate formed at −196 °C and (b) to the vapor species trapped in a nitrogen matrix at ca. 20 K; the results are illustrated in Figure 9 and listed in Table VIII. The spectrum includes features at 2800–3000, 1300–1500, 568, and 513 cm^{-1}, which attest to the presence of the Et_2Ga moiety (cf. $[Et_2GaF]_3$ and $[Et_2GaCl]_2$[53]). The absence of any strong bands in the region 1800–2000 cm^{-1} rules out terminal Ga–H bonds, but the appearance of strong bands at 1234 and 1162 cm^{-1} in the matrix spectrum is strongly suggestive of the binuclear unit $Ga(\mu\text{-}H)_2Ga$. Annealing the matrix causes these bands to decay and give way to a broad band centered near 1660 cm^{-1} so that the resulting spectrum resembles that of the neat solid at −196 °C. The obvious parallels with the behaviors of dimethylgallane[12] and gallane itself give us to believe that the vapor species is the dimer $[Et_2GaH]_2$ (cf. III) with a Ga–H–Ga bond angle in the order of 93°,[13b] but that a higher oligomer, $[Et_2GaH]_n$ where $n \geq 3$, is formed in the condensed phases at low temperatures. The identification of diethylgallane is verified by the ^1H and ^{13}C NMR spectra of a toluene-d_8 solution at ca. −40 °C. The ^1H spectrum comprises three resonances, viz., a broad singlet at δ 2.83, a triplet at δ 1.29, and a quartet at δ 0.76. The first of these is characteristic of protons bound to gallium,[21] and the shift is consistent with a Ga–H–Ga moiety (cf. $[Me_2GaH]_n$ δ 3.06[12]), whereas the triplet arises from the CH_3 and the quartet from the CH_2 protons of the Et_2Ga fragment [$J(CH_3–CH_2)$ = 8 Hz]. The ^{13}C spectrum displays a quartet at δ 11.7 and a triplet at δ 5.2 due to the carbon atoms of the CH_3 and CH_2 groups, respectively [J(C–H) = 125 Hz in both cases].

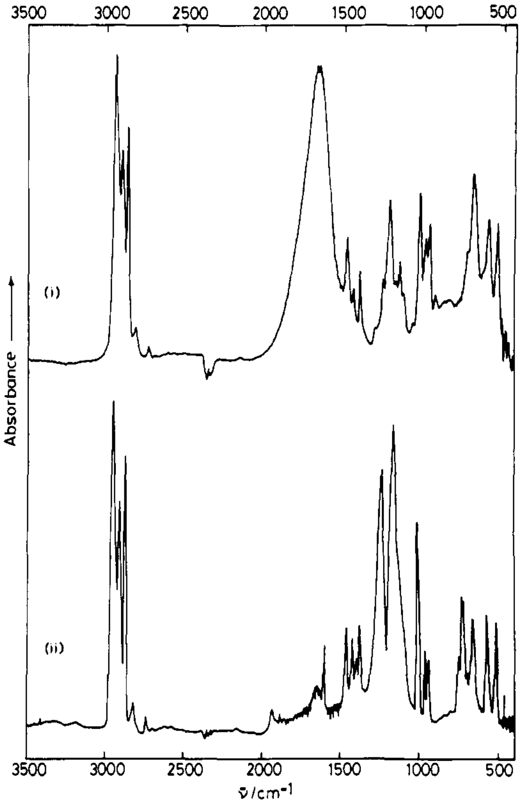

Figure 9. The IR spectra of diethylgallane in the forms (i) of the annealed solid condensate formed at 77 K and (ii) of the vapor species trapped in a nitrogen matrix at ca. 20 K.

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Table IX. Nozzle-to-Plate Distances, Weighting Functions, Correlation Parameters, Scale Factors, and Electron Wavelengths

nozzle-to-plate distance (mm)	Δs (nm^{-1})	s_{min} (nm^{-1})	sw_1 (nm^{-1})	sw_2 (nm^{-1})	s_{max} (nm^{-1})	correlation, p/h	scale factor, k[a]	electron wavelength (pm)[b]
259.80	2	20	40	122	144	0.1863	0.760 (22)	5.671
201.22	4	40	60	180	212	0.3923	0.764 (34)	5.671

[a] Figures in parentheses are the estimated standard deviations of the last digits. [b] Determined by reference to the scattering pattern of benzene vapor.

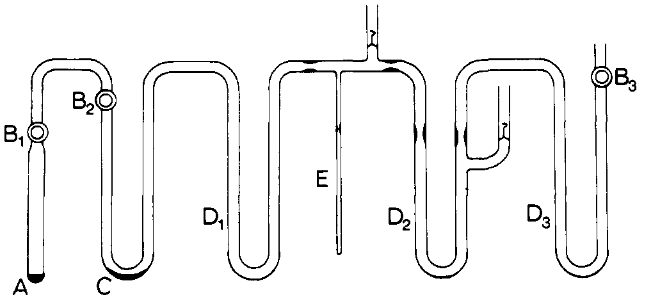

Figure 10. Pyrex glass apparatus used for the synthesis and sampling of gallane: (A) sample of $[H_2GaCl]_2$, (B_1, B_2, and B_3) greaseless valves, (C) freshly prepared $LiGaH_4$, (D_1, D_2, and D_3) U-tube traps for fractionation of volatile products, (E) NMR tube.

In a very recent report,[54a] Grady et al. have described the ^{1}H NMR spectrum of a mixture of triethylgallane and a component they identify as diethylgallane (produced by the IR-laser-powered pyrolysis of triethylgallane vapor). The interpretation of their spectrum is complicated by the overlapping of the ethyl group resonances of the two compounds, but, insofar as comparisons can be made, their results tally with ours. Grady et al.[54a] and also Eisch in an earlier report[54b] suggest that diethylgallane disproportionates "over a period of time". Our experience does not support this suggestion, and diethylgallane appears in our hands to be long-lived at room temperature, always provided that it is contained in all-glass apparatus which has been rigorously preconditioned.

Experimental Section

Synthesis of Gallane. All-glass apparatus, typically having the form illustrated in Figure 10, was rigorously preconditioned by heating under continuous pumping. In a representative experiment, monochlorogallane (ca. 200 mg, 1.9 mmol of H_2GaCl), itself prepared by the metathesis of gallium(III) chloride with an excess of trimethylsilane at ca. −23 °C,[11] was co-condensed with freshly prepared[18] lithium tetrahydridogallate (300 mg, 3.7 mmol) at −196 °C. Careful warming of the mixture to temperatures of −30 to −23 °C induced a reaction with the deposition of a gray or black deposit of elemental gallium. With all parts of the glassware to which the vapors had access cooled to temperatures <−20 °C in a stream of cold nitrogen gas, the volatile products were removed under continuous pumping and fractionated between traps held initially at −63 and −196 °C. These products included substantial quantities of elemental hydrogen and also a condensable fraction, shown to be gallane, $[GaH_3]_n$, which collected as a white solid, mainly in the trap at −196 °C. A minor proportion of this fraction was commonly retained, together with unchanged monochlorogallane and possibly hydride-rich chlorogallanes like Ga_2H_5Cl, by the trap at −63 °C, but warming to −45 °C resulted in rapid vapor transfer to the colder trap. When the evolution of volatile products had ceased, the sample of gallane was isolated by sealing the trap at the relevant constrictions; the sample was kept at −196 °C until required, access to it being regained by way of a suitable break-seal. The authenticity of such a sample was checked by reference to its melting point (ca. −50 °C), vapor pressure (ca. 1 mmHg at −63 °C), the IR spectrum of the vapor or of the solid condensate it forms at −196 °C (q.v.), or the ^{1}H NMR spectrum of the compound in toluene-d_8 solution at low temperatures (q.v.). The gallane amounted to ca. 14 mg (0.19 mmol of GaH_3), representing a yield of 10% based on eq 4 and the amount of monochlorogallane taken. The perdeuterated version of gallane was prepared in an analogous manner from $[D_2GaCl]_2$[11] and $LiGaD_4$.

Chemical Analysis of Gallane. A sample of gallane was allowed to decompose at room temperature with the deposition of gallium metal on the walls of the ampoule, the temperature being raised latterly to 90 °C to ensure complete decomposition to the elements. The hydrogen was removed and estimated to be 0.304 mmol by means of a Toepler pump, the solid residue being heated to induce desorption of the last traces of occluded gas. Analysis showed that the involatile residue consisted of gallium (0.167 mmol) free from detectable chloride impurity. That the proportion H_2:Ga should thus be 1.82:1, instead of 1.5:1 as required by eq 5, can be explained by the intervention of side-reactions such as that represented by eq 6.

In a second experiment, an excess of hydrogen chloride (3.752 mmol) was co-condensed with a sample of gallane at −196 °C. After 1 h at −95 °C, the volatile materials were withdrawn and assayed, while the white residue involatile at −20 °C was analyzed for gallium and chlorine. The results of the analysis set out below established, within the limits of experimental uncertainty, that reaction occurs in accordance with eq 7, thereby validating the empirical formula GaH_3 for the gallane.

	HCl consumed	H_2 evolved	Ga in residue	Cl in residue
found/mmol	0.360	0.356	0.118	0.364
proportions	3.05	3.02	1.00	3.09

Spectroscopic Measurements. IR spectra were recorded using one of four spectrometers, viz., a Perkin-Elmer Model 580A dispersive (4000–200 cm^{-1}), a Mattson "Polaris" FT-IR (4000–400 cm^{-1}), a Mattson "Galaxy" FT-IR (4000–400 cm^{-1}), or, for gas-phase studies at higher resolution, a Nicolet 7199 FT-IR instrument with a cooled Hg–Cd–Te detector and a KBr beam-splitter (4000–600 cm^{-1}). Solid noble gas or nitrogen matrices, typically at dilutions estimated to be ca. 1:200, were prepared by continuous codeposition of the gallane vapor (conducted via appropriately cooled, preconditioned glass tubing) with an excess of the matrix gas on a CsI window cooled to ca. 20 K by means of a "Displex" closed-cycle refrigerator (Air Products Model CS 202); fuller details of the relevant equipment and procedures are given elsewhere.[55] Raman spectra of solid samples were excited at λ = 514.5 nm with the output of a Spectra-Physics Model 165 Ar$^+$ laser and measured with a Spex Ramalog 5 spectrophotometer operating in conjunction with a Glen-Creston SCADAS data-handling system; the resolution was normally ca. 5 cm^{-1}. Solid films of volatile materials were presented for spectroscopic analysis by allowing the vapor to condense on a CsI window (for IR measurements) or a copper block (for Raman measurements) contained in an evacuated glass shroud and maintained at −196 °C. ^{1}H NMR measurements on toluene-d_8 or benzene-d_6 solutions at low temperatures were made at 250 MHz with a Bruker Model AM 250 or at 300 MHz with a Bruker Model AM 300 or WH 300. ^{13}C Measurements were made at 75.5 MHz with the Model AM 300.

Electron-Diffraction Measurements. The Edinburgh gas diffraction apparatus provided the basis of the electron-diffraction measurements, the patterns being recorded on Kodak Electron Image plates.[56] To accommodate the reactivity and thermal frailty of the gallane, we avoided both valves and joints by constructing a special all-glass inlet assembly. As illustrated in Figure 11, this provided for the direct injection of the gallane vapor from a storage ampoule into the chamber of the diffraction apparatus via a glass channel which could be suitably preconditioned and then cooled to temperatures in the range −15 to −20 °C to forestall thermal decomposition. The plates were washed after exposure and left exposed to air for 24 h before being developed in order to minimize the inescapable fogging effects produced by reaction of the gallane vapor with the photographic emulsion.[11,12,19,30] The precise nozzle-to-plate distances and electron wavelengths were determined from scattering patterns for benzene vapor recorded immediately after the sample pattern (see Figure 11). Details are given in Table IX, together with the weighting functions used to set up the off-diagonal weight matrices, the correlation parameters, and final scale factors.

Details of the electron-scattering patterns were collected in digital form using a computer-controlled Joyce-Loebl MDM6 microdensitome-

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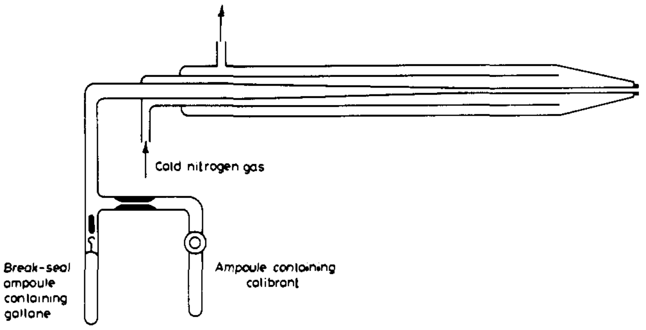

Figure 11. All-glass inlet system used for the admission of gallane vapor to the chamber of the electron-diffraction apparatus.

ter with the scanning program described previously.[57] Calculations made use of well-established programs for data reduction[57] and least-squares refinement,[35] the complex scattering factors being those listed by Fink and Ross.[58]

Chemical Studies and Reagents. The thermal instability of gallane made it impossible to determine the mass of a sample prior to any chemical reaction. Hence it was necessary, as in the experiment with HCl (q.v.), to treat the sample with a measured quantity of the reagent, judged to be in excess, under the appropriate conditions, then to separate and identify the components of the reaction mixture (typically on the basis of their vibrational and/or NMR spectra), and, where appropriate, to assay one or more of these components (e.g., by manometric measurements or elemental analysis). The reaction itself was carried out in a preconditioned all-glass ampoule equipped with a break-seal, in accordance with the sort of procedures that were adopted for the synthesis and isolation of the gallane (q.v.); subsequent manipulation and analysis of the reaction mixture could usually be accomplished using a more conventional vacuum line having a distillation train and greased ground-glass or, if necessary, greaseless stopcocks as well as ground-glass joints lubricated typically with Apiezon L grease. In none of the experiments was there any evidence that unchanged gallane survived the encounter with an excess of the reagent (HCl, NMe_3, NH_3, PH_3, or C_2H_4) under the conditions outlined in the preceding section.

All noncondensable gases—Ar, Kr, and N_2 (research grade)—were used as received from the British Oxygen Co. (B.O.C.). The following reagents, from the commercial sources indicated, were purified before use by fractionation in vacuo: HCl (Air Products), NH_3 (B.O.C.), and C_2H_4 (B.O.C.). Toluene-d_8 and benzene-d_6, both supplied by Aldrich, were dried and fractionated in vacuo prior to use as NMR solvents. Phosphine was prepared by the action of aqueous hydrochloric acid on calcium phosphide (Ventron), trimethylamine by the action of alkali on trimethylammonium chloride (Aldrich); fractional condensation of each of these reagents in vacuo gave a sample judged to be pure by the criteria of tensimetric and IR measurements.

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Spectroscopic Studies of the Non-Heme Ferric Active Site in Soybean Lipoxygenase: Magnetic Circular Dichroism as a Probe of Electronic and Geometric Structure. Ligand-Field Origin of Zero-Field Splitting

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Abstract: Ferric active sites are found in non-heme, non-iron–sulfur enzymes performing a variety of biological functions often involving dioxygen activation. Soybean lipoxygenase (SBL) is an important member of this class catalyzing the hydroperoxidation of unsaturated lipids. The purpose of this study is to use the combination of EPR and variable temperature variable field magnetic circular dichroism (MCD) to probe the ground and excited states in high-spin non-heme ferric enzymes. Low-temperature MCD is used to observe the low-energy spin-forbidden ligand-field excited states that are not obscured by higher energy charge transfer (CT) transitions. Parallel studies on ferric model complexes and predictions of *C*-term signs and transition energies are presented which enable the ferric geometry to be estimated from these ligand-field spectral features. Saturation magnetization of the MCD bands associated with CT transitions provides polarization information and thus the orientation of the ligand–Fe(+3) bonds relative to the **g** tensor of the ground doublet which is determined by the zero-field-splitting (ZFS) tensor. Variable-temperature EPR and MCD are used to obtain the ground-state ZFS which is analyzed in terms of the ligand field at the Fe(+3) site. Here we extend our earlier treatment of distorted tetrahedral complexes (Deaton, J. C.; Gebhard, M. S.; Koch, S. A.; Millar, M.; Solomon, E. I. *J. Am. Chem. Soc.* **1988**, *110*, 6241) to distorted octahedral and five-coordinate complexes. Together the saturation magnetization MCD and ZFS analyses enable one to obtain the orientation of specific chromophoric ligands at the active site. This is used to probe both endogenous and exogenous ligand to Fe(+3) CT transitions and provides significant geometric information. Studies of Fe(+3)–SBL show that oxidation of the octahedral Fe(+2) site produces little change in the coordination sphere of the iron center, which likely has at least two histidine ligands in a cis configuration which define the equatorial plane. OCN^- and N_3^- bind to the ferric active site producing rhombic EPR signals which parallel those observed upon hydroperoxide product addition to ferric enzyme. The MCD studies of the associated CT transitions define exogenous ligand interactions with the ferric SBL active site which are of relevance to the catalytic mechanism.

Introduction

Mononuclear non-heme iron centers are known or believed to be present in the catalytic active site of a large number of enzymes involved in reactions with dioxygen. These enzymes include the following: soybean lipoxygenase (SBL, hydroperoxidation of unsaturated lipids),[1a] Fe superoxide dismutase (SOD, dismutation

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