

Monochlorogallane: Synthesis, Properties, and Structure of the Dimer $\text{H}_2\text{Ga}(\mu\text{-Cl})_2\text{GaH}_2$ in the Gas Phase as determined by Electron Diffraction

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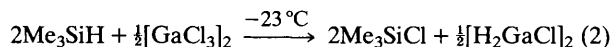
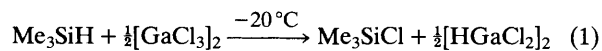
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Monochlorogallane, synthesised by metathesis involving gallium(III) chloride and trimethylsilane, has been characterised by its spectroscopic and chemical properties; electron diffraction has established the structure of the dimer $\text{H}_2\text{Ga}(\mu\text{-Cl})_2\text{GaH}_2$, the predominant vapour species at low pressure.

Unco-ordinated gallanes have proved remarkably elusive.¹ Reasonably well-authenticated derivatives appear to be confined to the disubstituted species $[\text{HGaX}_2]_2$ ($\text{X} = \text{Cl}$ or Br),² $[\text{R}_2\text{GaH}]_n$ ($\text{R} = \text{Me}$, $n = 2$;³ $\text{R} = \text{Et}$;⁴ $\text{R} = \text{Bu}^i$),⁵ and $\text{HGa}(\text{BH}_4)_2$.⁶ According to one report,⁷ monochlorogallane, formulated as $[\text{H}_2\text{GaCl}]_n$, is displaced from $\text{Me}_3\text{N}\cdot\text{GaH}_2\text{Cl}$ by the action of BF_3 . Little headway was made, however, with the characterisation of the product and, in the light of the doubts cast on the analogous preparation of gallane itself,⁸ there must be serious reservations about this claim. Here we outline the synthesis and physical and chemical characterisation of monochlorogallane.

It is well established that dichlorogallane, $[\text{HGaCl}_2]_2$, is produced in accordance with equation (1).² Following reaction of trimethylsilane in 5–10-fold excess with powdered gallium(III) chloride at -23°C , fractionation of the volatile products *in vacuo* gives a viscous colourless liquid (m.p. ca. -90°C ; v.p. at 20°C ca. 0.5 mmHg†). To secure reproducible results, however, it is necessary rigorously to exclude moisture, grease, or other contaminants, with short distillation paths, minimal use even of greaseless valves, and preconditioning of all glassware (by heating under continuous pumping). In these conditions the yield is typically ca. 80% based on equation (2). Decomposition occurs over a period of days at room temperature; the resulting quantitative formation of equimolar quantities of H_2 and an involatile white solid having the composition GaCl provides a means of analysis.



The i.r. and Raman spectra indicate that the compound exists as the dimer $\text{H}_2\text{Ga}(\mu\text{-Cl})_2\text{GaH}_2$ in both the condensed and vapour phases. For example, the i.r. spectrum of a solid film at 77 K includes the following absorptions in the range $3000\text{--}200\text{ cm}^{-1}$: 2020s, 1990sh, 678vs, 575m, 480mw, 382m, 290wsh, 265s (wavenumbers in cm^{-1} ; s = strong, m = medium, w = weak, v = very, sh = shoulder); an argon matrix gives the same pattern of bands at similar or identical wavenumbers. By measuring the vibrational spectra of the corresponding deuteriated compound, we have been able to accumulate sufficient information, not only to work out a more-or-less complete vibrational assignment, but also to perform a normal co-ordinate analysis for the molecules $\text{H}_2\text{Ga}(\mu\text{-Cl})_2\text{GaH}_2$ and $\text{D}_2\text{Ga}(\mu\text{-Cl})_2\text{GaD}_2$ on the assumption that each conforms to D_{2h} symmetry. The two i.r. bands near

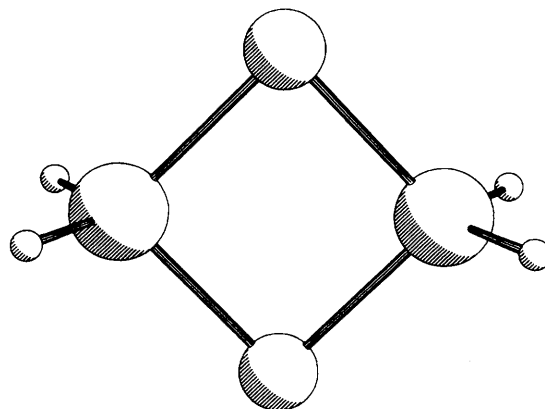


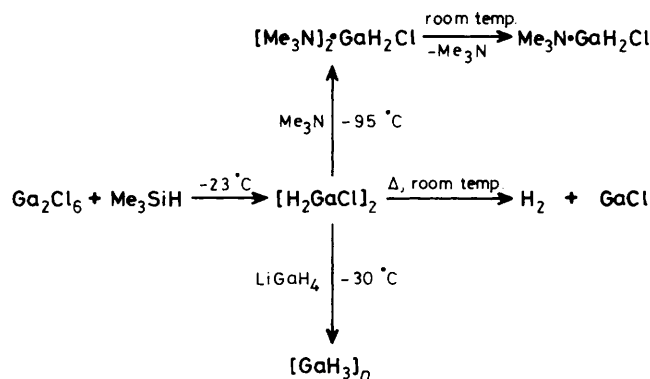
Figure 1. Perspective view of the molecule $\text{H}_2\text{Ga}(\mu\text{-Cl})_2\text{GaH}_2$ in the optimum refinement of the electron-diffraction analysis.

† 1 mmHg $\approx 13.6 \times 9.8$ Pa.

Table 1. Geometrical (r_a) and vibrational parameters for the gaseous molecules $X_2Ga(\mu-Cl)_2GaX_2^a$ ($X = H, ^b Me, ^c$ or Cl^d).

Parameter ^e	Distance/pm or angle/°			Parameter ^e	Vibrational amplitude/pm	
	$H_2Ga(\mu-Cl)_2GaH_2$	$Me_2Ga(\mu-Cl)_2GaMe_2$	$Cl_2Ga(\mu-Cl)_2GaCl_2$		$H_2Ga(\mu-Cl)_2GaH_2$	$Me_2Ga(\mu-Cl)_2GaMe_2$
$r(Ga \cdots Ga)$	324.1 (0.7)	332.8 (1.9)	330.1 (1.2)	$u(Ga \cdots Ga)$	8.6 (0.7)	11.5 (0.7)
$r(Ga-Cl_b)$	234.9 (0.3)	238.2 (0.4)	230.0 (0.1)	$u(Ga-Cl_b)$	7.1 (0.3)	9.6 (0.1)
$r(Ga-X_t)$	X = H, 155.9 (1.9)	X = C, 194.8 (0.3)	X = Cl, 209.9 (0.1)	$u(Ga-X_t)$	X = H, 9.2 ^f	X = C, 6.7 (0.3)
$\angle Cl_b-Ga-Cl_b$	92.8 (0.8)	91.4 (0.9)	88.3 (0.4)			
$\angle X_t-Ga-X_t$	X = H, 120 ^f	X = C, 135.4 (2.7)	X = Cl, 124.6 (0.9)			

^a Estimated standard deviations given in parentheses. ^b This work. ^c Ref. 12. ^d Ref. 13. ^e Subscript b = bridging, t = terminal. ^f Fixed.

**Scheme 1**

2000 cm^{-1} can thus be identified with symmetric and antisymmetric $\nu(Ga-H)$ modes and the intense band near 680 cm^{-1} with a GaH_2 scissoring mode. The 1H n.m.r. spectrum of the gallane dissolved in $C_6D_5CD_3$ at 20 °C consists of a single broad resonance centred at δ_H 5.24, a shift characteristic of terminal $Ga-H$ units. The resonance sharpens appreciably, but the spectrum is otherwise unchanged, when the solution is cooled to $-50^\circ C$.

Electron-diffraction patterns of the monochlorogallane vapour were recorded photographically on the Edinburgh apparatus⁹ with sample and nozzle at 50 °C; despite severe problems of fogging caused by reaction of the vapour with the photographic emulsion, processing¹⁰ and analysis^{9,11} of the data were accomplished by the procedures described previously. The scattering can be satisfactorily interpreted, like the vibrational properties, on the basis of a molecule $H_2Ga(\mu-Cl)_2GaH_2$ with D_{2h} symmetry, as illustrated in Figure 1. Those amplitudes of vibration which did not yield to refinement have been fixed at values calculated on the basis of the force field derived from the vibrational spectra. Hence the structure could be refined to give $R_G = 0.128$. The main parameters of interest are listed, together with those for the analogous molecules $Me_2Ga(\mu-Cl)_2GaMe_2$ ¹² and $Cl_2Ga(\mu-Cl)_2GaCl_2$,¹³ in Table 1. The $Ga-H$ distance is typical of a terminal $Ga-H$ bond (cf. $r(Ga-H) = 149-157$ pm for $Me_3N \cdot GaH_3$,^{14a} $HGa(BH_4)_2$,^{14b} and $[H_2GaNMe_2]_2$,^{14c}), and significantly shorter than the bridging $Ga-H$ bond in $Me_2Ga(\mu-H)_2GaMe_2$ (170.8 pm).³ The $Ga \cdots Ga$ distance in the chlorogallane is comparable with, but somewhat shorter than, those in $[Me_2GaCl]_2$ and Ga_2Cl_6 ; it is still substantially longer than twice the covalent radius of gallium and the corresponding distance in $Me_2Ga(\mu-H)_2GaMe_2$ (261.0 pm).³

The chemistry of monochlorogallane is in the process of being charted. The results of preliminary experiments are incorporated in Scheme 1. With trimethylamine the gallane reacts at $-95^\circ C$ to form the 2 : 1 adduct $[Me_3N]_2 \cdot GaH_2Cl$; this

dissociates at room temperature to the 1 : 1 adduct $Me_3N \cdot GaH_2Cl$ ⁷ and free NMe_3 . More compelling, however, is the role of monochlorogallane as a potential precursor to the elusive binary hydride $[GaH_3]_n$, with the important advantages that reduction is already two-thirds complete and that the compound is a liquid even at quite low temperatures. Indeed it reacts with $LiGaH_4$ at $-30^\circ C$ to produce a very volatile gallane with the composition GaH_3 which decomposes at temperatures in excess of $-10^\circ C$ to gallium metal and H_2 . The spectroscopic properties of this product, to be reported shortly,¹⁵ point to Ga_2H_6 , a diborane-like molecule, as the predominant species in the vapour and solution phases.

We thank Dr. S. Cradock for carrying out the vibrational amplitude calculations on the basis of the vibrational properties outlined here, and the S.E.R.C. for studentships (to M. J. G. and C. R. P.) and financial support of the Edinburgh electron-diffraction service (including a research assistantship to H. E. R.).

Received, 26th January 1988; Com. 8/00283E

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