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SPECTROSCOPIC ANALYSIS OF THE SOLID STATE STRUCTURES OF THE ARYLGALLIUM HALIDES, $(C_6H_5)_nGaX_{3-n}$ (X = Cl, Br, I)

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Summary

The complete series of arylgallium halides, $(C_6H_5)_nGaX_{3-n}$, $n = 1, 2$ for X = chloride, bromide, and the here-to-fore unreported iodides, has been prepared. The IR and Raman spectra, mass spectra, and, where possible, the ^{69,71}Ga nuclear quadrupole resonance spectra are all consistent with the existence of discrete, halogen-bridged molecular dimers in the solid state for each compound. The dioxane adducts of the chloride series, $(C_6H_5)_nGaCl_{3-n}$ · dioxane were prepared and examined as a further indication of the validity of these structural assignments. In these donor—acceptor adducts the Ga—Cl modes are characteristic of terminal bonds.

Introduction

In the course of characterizing the arylindium halides [1] it was desirable to prepare the arylgallium halide compounds, $(C_6H_5)_nGaX_{3-n}$, for comparison. No solid state structural characterization of these compounds appears to have been published, although the series $(C_6H_5)_nGaX_{3-n}$, $n = 1, 2$ and X = Cl, Br is known to be dimeric in benzene solution [2]. In this type of compound, however, it cannot be tacitly assumed that the solution phase structure is also the structure in the solid state. For example, the organoindium halides are often monomeric [3] or dimeric [4] in benzene, while dimeric or polymeric structures appear to exist in the solid state [1,5—7]. In order to gain solid state information, the arylgallium halides, $(C_6H_5)_nGaX_{3-n}$, $n = 1, 2$ and X = Cl, Br, I were examined by vibrational and mass spectrometry and, in so far as was possible, by ^{69,71}Ga nuclear quadrupole resonance spectroscopy.

The two compounds $C_6H_5GaI_2$ and $(C_6H_5)_2GaI$ appear not to have been reported previously. Perkins and Twentyman [2] synthesized the series $(C_6H_5)_n$-

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GaX_{3-n}, $n = 1, 2$; $X = Cl, Br$, using triphenylgallium in reaction with HX, X_2 and GaX_3. Viktorova [8] also used the $(C_6H_5)_3Ga—GaCl_3$ redistribution reaction to prepare the chloride series. Schmidbaur and Findeiss [9] reacted $(CH_3)_3SiC_6H_5$ with GaX_3, $X = Cl, Br$, to prepare $C_6H_5GaX_2$. Wilkinson and Worrall prepared alkylgallium iodides by reaction of "GaI" with alkyl iodides or Ga, I_2 and RI as a direct reaction [10]. In the present work the entire series of six arylgallium halide compounds was prepared, in some cases by the redistribution of $(C_6H_5)_3Ga$ and GaX_3, and in others by reaction of $(C_6H_5)_3Ga$ and X_2.

Experimental

Syntheses

The air and moisture sensitivity of the arylgallium halides was found to be even greater than that of the corresponding arylindium halides [1]. Accordingly, all manipulations were carried out in Schlenk tubes or in a dry box. Reagents were mixed in the appropriate stoichiometric ratio in all cases.

Gallium trichloride (ROC/RIC) was used without further purification. Gallium tribromide and triiodide were prepared according to methods described by Brauer [11]. Hydrocarbon solvents were refluxed over P_2O_5 while being degassed with N_2 and then distilled.

Phenylgallium dichloride. This compound was prepared in 30% yield by the procedure of Perkins and Twentyman [2] and purified by sublimation in vacuo; m.p. 123—125°C (lit. [2] 122—123°C).

Diphenylgallium chloride. Triphenylgallium (0.0167 mol) and 0.0083 mol of gallium trichloride were placed in a 50 ml Schlenk flask, evacuated, and heated at 150°C for 12 h. The resulting reaction mixture was boiled with benzene, filtered, diluted with an equal volume of hexane and allowed to cool. Colorless needles of diphenylgallium chloride were collected and washed with hexane; m.p. 194—196°C (lit. [2] 197°C). A 77% yield based on the combined amounts of starting materials was obtained.

Phenylgallium dibromide. Triphenylgallium (0.0167 mol) and 20 ml of benzene were placed in a 50 ml Schlenk flask. Bromine (0.0332 mol) in 20 ml of benzene was added dropwise. The solvent was removed under vacuum and the resulting solid was sublimed twice in vacuo, yielding a small amount of colorless, crystalline phenylgallium dibromide; m.p. 134—135°C (lit. [2] 129—130°C). The yield was about 30%.

Diphenylgallium bromide. This compound was prepared according to the procedure of Perkins and Twentyman [2], but recrystallized from benzene; m.p. 223—225°C (lit. [2] 219—220°C). The yield was about 80%.

Phenylgallium diiodide. Triphenylgallium (0.0032 mol) and 0.0064 mol of gallium triiodide were placed in a 50 ml Schlenk flask along with 30 ml of benzene and refluxed for 12 h. The resulting pale yellow solution was cooled and the solvent removed under reduced pressure yielding a yellow, low-melting solid which was boiled with hexane and filtered. After several days, pale yellow crystals formed which were warmed gently with 20 ml of n-pentane containing a little cyclohexane. After filtering, the volume was reduced by vacuum evaporation and small colorless crystals of phenylgallium diiodide formed; m.p. 86—87°C. The yield was about 20%.

Diphenylgallium iodide. Triphenylgallium (0.0167 mol) was treated with 0.0167 mol of iodine in benzene in a procedure similar to that described above for $(C_6H_5)_2GaBr$. Instead of benzene, cyclohexane was used for recrystallization, yielding 0.0140 mol of colorless leaflets of diphenylgallium iodide, m.p. 191—192°C. This corresponds to a yield of 84% based on triphenylgallium as the limiting reagent.

Dioxane adducts. Dioxane adducts were prepared as described before for indium adducts [1]. Weighed samples of each adduct were decomposed by heating in vacuo at 100°C for several hours to determine stoichiometry, and all were found to be 1/1 adducts.

Analyses

The extreme air and moisture sensitivity of the arylgallium halides made it difficult to obtain reliable elemental analyses using the facilities available. Instead, high resolution mass spectra of the compounds were used for analytical purposes. No evidence of impurities was found in any of the spectra. The achievement of sharp constant melting points on multiply recrystallized samples was also used as evidence of purity.

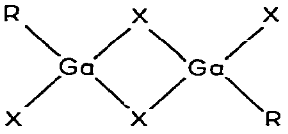
Vibrational spectra. Infra-red spectra were measured on a Perkin—Elmer Model 180 double-beam grating spectrophotometer between 1200—180 cm^{-1}. Samples were run as Nujol mulls suspended between CsI plates and were prepared in a dry box. Raman spectra were obtained on compounds sealed inside Kimex capillary tubes using a Spex Ramalog 1401 double-monochrometer spectrometer. A CRL Model 54 Ar^+ laser was used for excitation and operated at 150 mW power and 4880 Å. Frequency errors are estimated to be about ± 2 cm^{-1}.

Mass spectrometry. Electron impact mass spectra were obtained on a CEC (DuPont) 21-110B mass spectrometer at 70 eV ionizing voltage and 6 kV accelerating voltage. The methane CI spectra were obtained with the same spectrometer previously modified for high pressure operation [12,13]. The reagent gas pressure was typically 0.7—1.0 Torr, the accelerating voltage 6 kV, the ionizing voltage 400—600 eV, and the repeller voltage 0 V. The samples were introduced into the spectrometer by direct insertion with a source block temperature of 200—300°C and a sample temperature of 90—170°C.

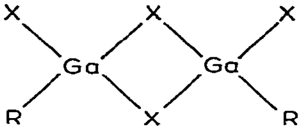
NQR spectra. The nuclear quadrupole resonance data were obtained on a spectrometer that has been described before [14]. Frequency measurements were made using spectrum analyzing techniques [15]. The data were gathered at room temperature and frequency errors of about 0.03 MHz could be incurred by improperly selecting the center-line of the resonance multiplet. Otherwise, errors are about 0.003 MHz. Gallium has two NQR active nuclei, ^{69}Ga and ^{71}Ga, which both have spin 3/2. ^{69}Ga is about 60% abundant and ^{72}Ga is 40% abundant. The frequency difference between them is simply given by the ratio of their quadrupole moment, i.e., 1.587 [16]. It is not possible to extract uniquely the nuclear quadrupole coupling constant and the asymmetry parameter from these simple frequencies. For $C_6H_5GaCl_2$, $\nu(^{69}Ga) = 29.32, 29.36$ MHz and $\nu(^{71}Ga) = 46.53, 46.58$ MHz.

Results and discussion

The vibrational spectra of the parent halides GaX_3, X = Cl, Br, I, in the solid state [17—20], in solution [17,18] and in the gas phase [19,21] are fully consistent with the halogen bridged dimeric structure of D_{2h} symmetry that is known to exist for $GaCl_3$ [22] and GaI_3 [23] based on X-ray diffraction. The nuclear quadrupole resonance spectra of GaX_3 compounds also give excellent evidence for this structure [24—26]. By analogy to the corresponding organoaluminum halides [27] one might expect that replacement of halogens by organic groups would lead to the following geometries for $RGaX_2$ and R_2GaX. $(CH_3GaCl_2)_2$ does indeed appear to have structure (Ia,b) in the solid state [28].



(Ia)



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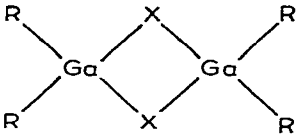

(II)

Thus, a reasonable starting point is to compare the spectra of the arylgallium halides to those of the gallium trihalides. However, considerable caution needs to be exercised because the C_6H_5—Ga motions often have symmetries and energies similar to those of the dimeric skeleton. The resultant coupling will be extensive. Perhaps because of this, there is more similarity in the vibrational spectra of $C_6H_5GaX_2$—$(C_6H_5)_2GaX$ pairs when X = Br, and I, than when X = Cl. If C—C mode coupling with the Ga—X framework is present, it should be greatest with the lighter halogen, chlorine. However, without a complete vibrational and normal coordinate analysis it is impossible to determine how all modes combine and shift. In spite of this difficulty, several general trends are observed in the frequency and intensity data in Table 1, but no extensive interpretation will be proposed.

As with the arylindium bond [1], pure Ga—C modes do not exist in these compounds. A consistent assignment of the modes that involve Ga—C motion coupled to ring motion can be extracted from comparisons with other monosubstituted benzenes [29] and the analogous arylindium halide [1] series. These modes are shown in Fig. 1 and need not be discussed in detail. The in-plane stretch at 660—675 cm^{-1} involves C—C and Ga—C stretching and the 10—25 cm^{-1} increase in its frequency compared to the indium compounds is consistent with more covalent Ga—C bonds compared to In—C bonds and/or a mass effect. Its frequency appears to be more sensitive to the number of halogens bonded to Ga than the type of halogen. This mode and the other in-plane stretch at 330—350 cm^{-1} may be mixed with skeletal stretching modes (ν_1, ν_8, ν_{11}, ν_{16}) [30].

In the low frequency region a series of Raman modes are found that are strongly X sensitive, vary in intensity as X changes and are not readily assignable to phenyl—Ga motions. In Fig. 2 are shown the modes ν_2 and ν_3 of a bridged dimeric skeleton [30]. These modes belong to the totally symmetric representation and are strongly Raman active [17—21]. ν_2 is the breathing mode

TABLE 1

VIBRATIONAL FREQUENCIES OF ARYLGALLIUM HALIDES IN THE SOLID STATE [a]

Compound	Metal sensitive phenyl modes					ν_2	ν_3	"Ga—Cl"	Other IR
	Mode A	Mode B	Mode C	Mode D	Mode E				
$GaCl_3$ [b]						330 m	167 m		
$C_6H_5GaCl_2$	675 w	405 vw	—	225 w	178 w	279 m	140 vs		446 s, 305 s,
				215 w			133 vs		279 s
$(C_6H_5)_2GaCl$	661 w	—	—	232 m	183 w	263 w	136 vs		448 s, 442 s
					175 w		125 vs		328 s, 248 s
$GaBr_3$ [b]						204 vs	119 vs		
$C_6H_5GaBr_2$	677 m	393 w	340 w	220 ms	203 w	185 s	139 vs		440 s, 328 s,
			333 w						275 s, 249 s
$(C_6H_5)_2GaBr$	665 m	403 w	—	234 m	—	185 s	142 vs		443 s, 328 s,
		393 w	—						249 s
GaI_3 [b]						143 vs	86 s		
$C_6H_5GaI_2$	667 w	—	355 w	246 w	200 mw	155 vs	90 s		440 s, 303 s,
					184 w				269 w
$(C_6H_5)_2GaI$	665 m	402 w	—	237 mw	205 w	150 vs	140 s, sh		448 s, 323 s,
				223 mw	179 w				252 s
$GaCl_3 \cdot$ dioxane								400 vs	
								336 vs	
$C_6H_5GaCl_2 \cdot$ dioxane	674 w	381 w [b]	—	232 w	—			377 s	
				220 w				280 m	
$(C_6H_5)_2GaCl \cdot$ dioxane	660 m	—	—	228 w	165 w			339 vs	290 m

[a] Raman frequencies unless otherwise noted. [b] Refs. 18—21.

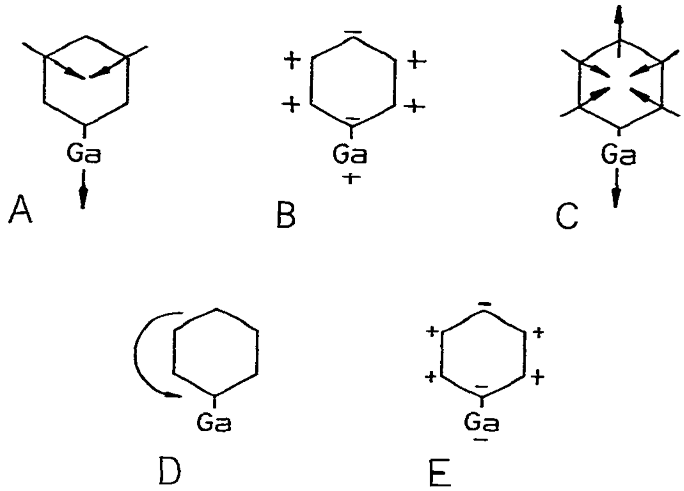

Fig. 1. Ga—C_6H_5 motions [29].

of the Ga_2X_2 ring in structures I and II and it should be strongly X sensitive. In $C_6H_5GaX_2$, X = Cl, Br, I bands at 279, 185 and 153 cm^{-1} appear and in $(C_6H_5)_2GaX$, a similar set of modes occurs at 263, 181 and 150 cm^{-1}. The intensity trend for these sequences is that which is expected for the Ga—X bond polarizability difference, namely Ga—Cl < Ga—Br < Ga—I. Further, in the GaX_3 compounds a set of modes having about the same frequency appear [18—21] and were assigned to ν_2 on the basis of normal coordinate analyses [18]. Consequently, it seems reasonable to assign these frequencies to ν_2 in the aryl-substituted compounds. Another set of modes located at lower frequency shifts more when the halogen is terminal ($C_6H_5GaX_2$ and GaX_3) than when a phenyl ring is terminal ($(C_6H_5)_2GaX$). Such behaviour would be expected of ν_3 and these bands are tentatively assigned to this motion in the aryl-substituted compounds by analogy to the GaX_3 compounds [18—21].

Although they appear to be consistent with the dimeric formulation, these vibrational spectra do not give a decisive structural picture when taken by themselves. The mass spectral and nuclear quadrupole resonance data offer further support for the existence of dimers, however. In addition to the expected fragmentation pattern, the CH_4 chemical ionization mass spectra of the $(C_6H_5)_nGaX_{3-n}$ series contain ions characteristic of the dimeric molecules in

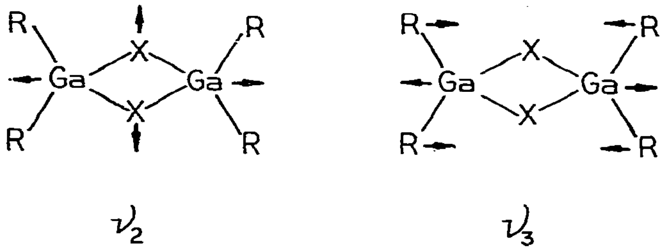

Fig. 2. Two metal-sensitive ring modes in the arylgallium halides.

TABLE 2

ELECTRON IMPACT MASS SPECTRAL DATA FOR ARYLGALLIUM CHLORIDES

Ions	Percentage of total ion current [a]	
	$(C_6H_5)_2GaCl$ [b]	$C_6H_5GaCl_2$ [c]
$GaCl_3^+$	0.00	0.77
$C_6H_5GaCl_2^+$	0.82	10.40
$(C_6H_5)_2GaCl^+$	7.44	0.21
$C_6H_5GaCl^+$	15.76	8.83
$(C_6H_5)_2Ga^+$	6.44	0.58
$C_6H_5Ga^+$	0.57	0.00
$GaCl_2^+$	0.00	6.62
$GaCl^+$	0.55	2.49
Ga^+	16.56	14.49
$C_{12}H_{10}^+$	7.42	0.23
$C_6H_6^+$	5.67	3.40
$C_6H_5^+$	17.17	15.54

[a] Isotopes for all nuclides except ^{13}C were summed in obtaining these data. The values were corrected for ^{13}C. Hydrocarbon fragments account for the remaining ions. [b] Source temperature was 170°C. [c] Source temperature was 100°C.

the solid state that are vaporized as such. High molecular weight ions containing two gallium atoms with 2 or 4 C_6H_5 rings and 1, 2, 3, or 4 halogen atoms appear. For example, in $(C_6H_5)_2GaCl$ the ion $(C_6H_5)_4Ga_2Cl^+$ is present and in $C_6H_5GaCl_2$, $(C_6H_5)_2Ga_2Cl_3^+$ and $(C_6H_5)_2Ga_2Cl_4^+$ are found. The bromide and iodide compounds produce similar ions. The 70 eV electron impact spectra are similar for all compounds so only the $(C_6H_5)_nGaCl_{3-n}$ series, $n = 1, 2$, is given in Table 2. The dimeric fragments are broken under these conditions so no high molecular weight species are seen. The data in Table 2 suggest that both symmetrical and unsymmetrical dimer cleavage occurs according to Fig. 3, although unsymmetrical cleavage is much less common. The temperatures required to obtain mass spectra of the gallium compounds are on the average about 100°C lower than for their indium counterparts [1]. Moreover, the organogallium halides can be sublimed which is suggestive of the existence of rather easily volatilized molecular units in the solid. The polymeric indium compounds cannot be sublimed.

Only $C_6H_5GaCl_2$ produced a nuclear quadrupole resonance spectrum. The $^{69,71}Ga$ NQR data for this compound are, however, interesting to compare with those of $GaCl_3$ and $(C_6H_5)_3Ga$ especially in light of the known ^{27}Al spectra for the bridged dimeric AlX_3, $C_6H_5AlX_2$ and $(C_6H_5)_3Al$ compounds [27]. Gallium, unlike Al, is an $I = 3/2$ nucleus and thus e^2Qq/h and η are not uniquely determinable. For an $I = 3/2$ nucleus, however, an asymmetry parameter of unity produces an increase in the resonance frequency of only 15% over the value at $\eta = 0$ [16]. Thus some very qualitative comparisons can be made between e^2Qq/h for ^{27}Al and the gallium resonance frequency even though η is likely to lie in the 0.4—0.7 range by comparison to the aluminum analogs [27]. Upon progressing from $AlBr_3$ to $C_6H_5AlCl_2$ to $(C_6H_5)_3Al$, the ^{27}Al coupling constant varies from 14 to 24 to 20 MHz [27]. In the series $GaCl_3$, $C_6H_5GaCl_2$, $(C_6H_5)_3Ga$, $\nu(^{71}Ga)$ ranges from 18 [24—26] to 29 to 49 MHz [31].

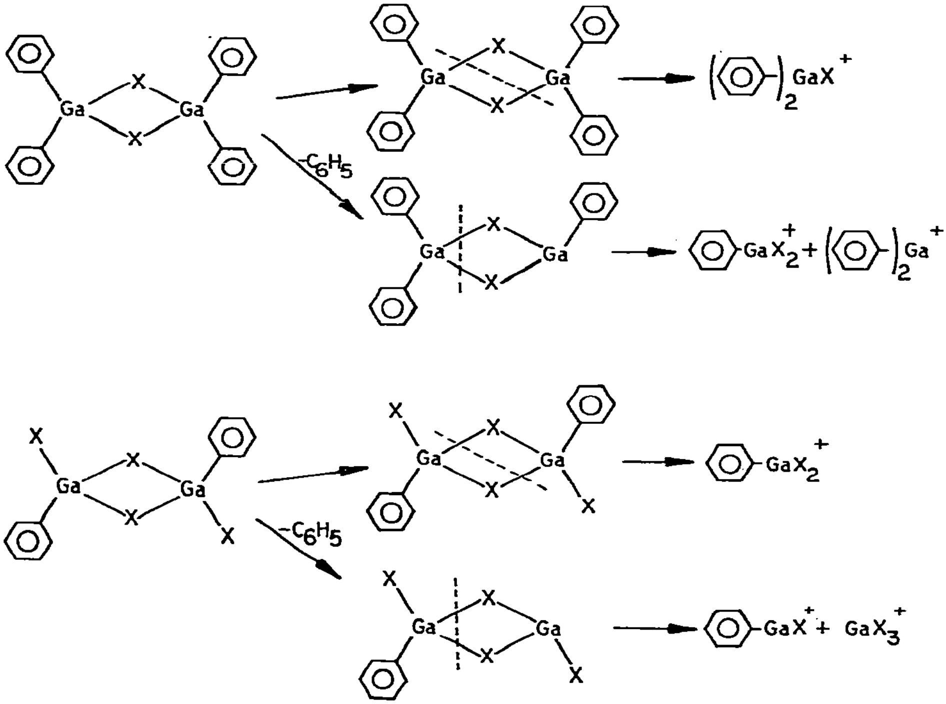

Fig. 3. Monomeric ion formation by symmetrical and unsymmetrical dimer cleavage.

Since the increase in the electric field gradient (EFG) at aluminum in $(C_6H_5)_2$-Al_2Br_4 compared to that in Al_2Br_6 is about the same as that observed when gallium is the metal, there is good evidence for structural similarity among these systems. $(C_6H_5)_3Ga$, on the other hand, contains associated monomeric units in the solid state [32], whereas $(C_6H_5)_3Al$ is a true bridged dimer [27]. The much lower EFG at ^{27}Al in $Al_2(C_6H_5)_6$ results from the approximately tetrahedral arrangement of carbon atoms about aluminum. Gallium is in a distorted five-coordinate field of carbon atoms in the solid, but, because of the trigonal planar arrangement of carbon atoms in the primary coordination sphere [32], a much larger field gradient is generated. The NQR data for $C_6H_5GaCl_2$ show that two crystallographically inequivalent Ga atoms are present in the solid state.

The dioxane adducts of the arylgallium chlorides were prepared in order to determine the changes in the vibrational spectra, particularly of the halogen motions, that accompany a breakdown of the molecular dimers in these compounds. In these complexes the acidic position of the gallium atom is coordinated by the Lewis base, L, rendering the Cl atoms terminal. Most $GaX_3 \cdot L$ compounds contain four-coordinate gallium in an approximately C_{3v} symmetry and have Ga—Cl frequencies falling in the range of 420—330 cm^{-1} [33—36]. In $GaCl_3 \cdot$ dioxane two modes appear in both the IR and Raman at about 403 and 336 cm^{-1}. The 403 cm^{-1} mode is broad in the IR and definitely split to 400 and 408 cm^{-1} in the Raman. These modes are very likely the e and a_1, Ga—Cl motions for C_{3v} molecular geometry in which the e mode is split by crystal packing forces. Since the a_1 mode is strongest in the Raman and rather weak in the IR, it is not possible to eliminate rigorously the chance that the gallium atom lies in a five-coordinate field in which crystal forces have caused the a_1 mode to become IR active, however. $C_6H_5GaCl_2 \cdot$ dioxane produces two modes at 377 cm^{-1} and 280 cm^{-1} that are strongly active in both the IR and Raman. The selection rules do not allow a distinction to be made in this case between four and five coordination because the stretching modes have the same activity for both. As expected for $(C_6H_5)_2GaCl \cdot$ dioxane a single mode at 339 cm^{-1} is found in both the IR and Raman. It is interesting to note that the highest energy Ga—Cl mode corresponding to asymmetric motion markedly decreases in frequency as the number of phenyl rings attached to gallium increases. No doubt this in part reflects an increase in the Ga—Cl bond ionic character as the gallium ionic charge is neutralized by the increasing number of phenyl rings. These Ga—Cl vibrational modes all have frequencies characteristic of "terminal" Ga—Cl bonds and indicate that the dimeric units are broken down by formation of donor—acceptor bonds with dioxane.

The evidence available on the arylgallium halides from vibrational, mass spectral, and nuclear quadrupole resonance measurements as well as the chemical properties of these compounds strongly suggests that discrete molecular dimers exist in the solid state. The arylgallium halides are thus structurally similar to the arylaluminum halides and do not resemble the polymeric arylindium halides.

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