

Chlorogallanes (GaClH_2 , GaCl_2H , and GaCl_3) and Their Dimer IsomersBrian J. Duke,[†] Tracy P. Hamilton, and Henry F. Schaefer III*

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The dimers of the three chlorides of gallium(III) have been studied by using ab initio quantum-mechanical methods at high levels of theory for these relatively large molecules. The problem of accurately predicting the geometry of the bridge region is investigated. Large basis sets (including f functions) and electron correlation are required to obtain the Ga-Cl_b distance correctly (b denotes bridging). Theoretical bond angles converge much more quickly with respect to level of theory, leading us to suggest that the experimental Ga-Cl_b-Ga angle of 87.2° for Ga₂Cl₂H₄ be revised slightly upward to 90°. The H-Ga-H angle is predicted to be 132°. The geometry and energy of all possible isomers of the monochloro- and dichlorogallane dimers are also reported, as well as those for Ga₂Cl₆. Agreement between theory and experiment for Ga₂Cl₆ is significantly better than for Ga₂Cl₂H₄. For each Cl on a bridging site, the dimerization energy (relative to an analogous molecule with a H at that site) is increased by 6-8 kcal mol⁻¹, and for each terminally bonded Cl the dimerization energy is decreased by 1-2 kcal mol⁻¹ relative to the analogous molecule with a H bonded at that position. Harmonic vibrational frequencies for the monochlorogallane dimer are predicted and compared well with the experimental infrared and Raman fundamentals.

Introduction

There has been considerable recent interest in bridged gallium compounds, particularly those with hydrogen bridges. The simplest species, digallane, has been synthesized by the Downs group at Oxford and its structure elucidated,¹ prompting research on digallane in several theoretical groups.²⁻⁴ The simplest chlorine derivative is monochlorogallane, which exists as the dimer, with chlorine rather than hydrogen bridges.⁵ The dimer of monochlorogallane is the smallest molecule containing gallium-chlorine bridge bonding. This compound is the precursor for the synthesis of digallane¹ and also galloborane.⁶

Dichlorogallane has also been synthesized⁷ and appears to spontaneously dimerize as well. Gallium trichloride, or trichlorogallane, forms a dimer with chlorine bridges. Both of these systems are large and therefore difficult to study with high-level ab initio theoretical methods. With large basis sets, it is not possible at present to use methods that include electron correlation or to evaluate second derivatives (and hence harmonic vibrational frequencies) for all of the dimers of chlorine-substituted gallanes. This study therefore focuses attention on the dimer of monochlorogallane, with some lower level results presented for the dimers of dichlorogallane and gallium trichloride.

For Ga₂Cl₂H₄, Lammertsma and Leszczynski (LL)⁸ previously used the ab initio Hartree-Fock method with the 3-21G* basis set.⁹ This is a modest basis set that might not be expected to give good agreement with experiment. Nevertheless, the results for Ga₂Cl₂H₄ are in much poorer agreement with experiment than found for digallane with the same basis set. In particular, the geometry of the bridge region is not well reproduced by theory,⁸ giving 3-21G* SCF Ga-Cl bond lengths which are too large by 0.059 Å, thus increasing the Ga-Ga distance to 0.214 Å. Hartree-Fock theory with the 3-21G* basis set predicts³ the Ga-Ga distances in the bridge region of Ga₂H₆ to be too long by 0.083 Å, so the digallane results are closer to experiment than in the case of Ga₂Cl₂H₄. For digallane, inclusion of electron correlation reduces the size of the four-membered ring by improving the description of the bridge bonding, and this is expected for Ga₂Cl₂H₄ as well. Given the discrepancy between the experimental and theoretical structures for Ga₂Cl₂H₄, we reexamined this problem with more complete basis sets and correlated methods. We also present theoretical structures and energetics for dimers of GaCl₂H and GaCl₃ for the first time.

Methods

The 3-21G basis set⁹ was the smallest used in this investigation. The 3-21G* basis set⁹ has a set of polarization d functions appended to both gallium and chlorine. Throughout this study, the d and f function sets used were the five-component and seven-component spherical harmonic Gaussians. Therefore our results will differ slightly from those of LL⁸

for the 3-21G* basis. The HUZ-SV** basis, used in an earlier Ga₂H₆ paper by Duke,⁴ consisted of the Huzinaga¹⁰ 4333/433/4 basis split to 43321/4321/4 with polarization d functions added for gallium and the standard 6-31G** basis set for chlorine and hydrogen. The d function orbital exponents on Ga were 0.207 for both the 3-21G* and the HUZ-SV** basis sets. This polarization exponent is that recommended by Huzinaga.¹⁰

The sp portion of the present basis set was improved by using contracted sets of double- ζ (DZ) quality based on the 14s11p primitive set for Ga and by using standard DZ and triple- ζ (TZ) sets for Cl and H. These basis sets were used as the foundation for the best basis sets employed, which included first and second polarization functions. The DZ basis set is the 14s11p5d/7s5p2d contracted set from Dunning¹¹ for Ga, with a 11s7p/6s4p set¹² on Cl and a 4s/2s set¹³ on H. A basis set of double- ζ plus polarization (DZP) quality was constructed by the addition of d functions of exponent 0.65 on Cl and 0.16 on Ga and p polarization functions of exponent 0.75 on H. For the gallium trichloride dimer, this basis set includes 212 functions.

For the largest sp basis on Ga, the outermost contracted primitives in the 14s11p5d/7s5p2d basis set were uncontracted until a 14s11p5d/10s8p2d contracted set was obtained. The latter basis set will be referred to as TZ, but is actually rather less than triple- ζ quality in the valence region. The TZ basis on Cl was the 12s9p/6s5p McLean-Chandler basis,¹⁴ and the Huzinaga-Dunning 5s/3s contracted set was used for H.¹³ These near-TZ sets were used in conjunction with two sets of polarization functions on each atom, as well as a single set of second polarization functions, to create the largest basis set used in this study. We will designate this basis as TZ2P+f even though it is TZ2P+d on H. The polarization exponents are 0.207 and 0.07 for Ga and are 1.5 and 0.375 for H and Cl, whereas the second polarization exponents are f functions with exponents 0.49 on Ga and 0.7 on Cl and d functions with exponent 1.0 on H. This basis set contained 254 functions when used for Ga₂Cl₂H₄.

The central methodology used for all systems is the Hartree-Fock self-consistent field molecular orbital method (SCF) with the determination of molecular geometries by the use of analytic first derivatives¹⁵

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Table I. SCF Results for the Equilibrium Geometry of the Monochlorogallane Dimer (Bond Distances, Å; Bond Angles, deg)

basis set	R-(Ga-Ga)	R-(Ga-Cl)	R-(Ga-H)	∠Cl-Ga-Cl	∠H-Ga-H
3-21G	3.644	2.452	1.554	96.0	132.8
3-21G*	3.455	2.406	1.571	91.8	132.4
HUZ-SV**	3.441	2.406	1.557	91.3	132.6
DZP	3.475	2.416	1.552	92.0	132.9
TZ2P+f	3.422	2.393	1.553	91.3	131.9
ECP-DZ	3.619	2.450	1.534	95.2	138.0
ECP-DZ+d	3.406	2.374	1.542	91.7	131.7
ECP-DZP	3.412	2.377	1.537	91.7	132.1
expt ⁵	3.241	2.349	1.559	87.2	

(except for the TZ2P+f SCF optimization which was done with finite displacements). Harmonic vibrational frequencies were evaluated at the SCF level by using analytic second derivatives for the monochlorogallane dimer.¹⁶ Predicted infrared (IR) intensities were obtained by using analytic dipole moment derivatives.

To investigate the effect of electron correlation, configuration interaction¹⁷ with all single and double excitations (CISD) from the valence orbitals was employed for the monochlorogallane dimer. However, CISD gradient optimization of the Ga₂Cl₂H₄ global minimum structure was only possible with the 3-21G* basis set due to disk and memory limitations. The resulting CISD wave function contained 71 437 configurations. Excitations from the core orbitals (1s, 2s, and 2p on Cl; 1s, 2s, 2p, 3s, and 3p on Ga) were not included in the CISD wave function.

An alternative method of determining electron correlation is second-order Moller-Plesset perturbation theory (MP2), and it was used to help gauge the further effects of electron correlation because MP2 is intermediate in quality between SCF and CISD. The same core orbitals as those mentioned above were also excluded from the MP2 wave function. Structures optimized at the 3-21G* MP2 level of theory were performed from pointwise energy calculations. MP2 generally overcorrects the SCF wave function for electron correlation, which is an important fact to remember in later discussion.

The effective core potential (ECP) method of Igel-Mann et al.¹⁸ was also employed in the preliminary stages of this research. The double- ζ (DZ) basis for the valence electrons is also from Igel-Mann et al.¹⁸ Adding a set of five-component d polarization functions to the valence basis sets of gallium and chlorine with exponents of 0.16 and 0.5, respectively, gives the ECP-DZ+d basis set. The ECP-DZP basis is similar but with p polarization functions with exponent 1.0 added on hydrogen. In addition to the intrinsic value of predictions made by using these ECP methods, they have a further important use. For molecules containing first-row atoms, the appropriate initial step, if the geometry is not known, is to explore the potential energy surface and estimate the Hessian by using the STO-3G basis set. A computation with a larger, more appropriate basis set can then be performed by using the geometry and Hessian from the STO-3G basis as initial values. For gallium, the STO-3G basis set is likely to be inadequate, so the ECP method provides a good initial strategy for gallium compounds, prior to searching for the minimum geometry with a large basis set all-electron method.

The TURBOMOLE¹⁹ and PSI²⁰ program suites were used for the aforementioned methods.

Results and Discussion

Geometry of the Monochlorogallane Dimer. The first stage of this investigation was to examine whether improved basis sets give a better representation of the Ga₂Cl₂H₄ geometry, particularly for the bridge region. The optimized SCF geometrical parameters for various basis sets are presented in Table I. All of these SCF values disagree with the electron diffraction experiments for the geometry of the bridge region. The inclusion of polarization functions is clearly important; the decrease in the Ga-Cl distance upon adding d functions to the 3-21G basis to give 3-21G* is 0.046 Å. The further decrease upon adding another set of polarization

Table II. Geometries of Ga₂Cl₂H₄ Showing the Effects of Electron Correlation Using the 3-21G* Basis Set (Bond Distances, Å; Bond Angles, deg)

level of theory	R-(Ga-Ga)	R-(Ga-Cl)	R-(Ga-H)	∠Cl-Ga-Cl	∠H-Ga-H
3-21G*/SCF	3.455	2.406	1.571	91.8	132.4
3-21G*/MP2	3.342	2.367	1.577	89.8	132.1
3-21G*/CISD	3.379	2.378	1.578	90.6	132.2

functions and a set of second polarization functions on each atom is 0.022 Å (approximately the difference between the DZP and TZ2P+f results). The Ga-Ga distance is a nonbonded distance and is therefore dependent on both the Ga-Cl_b-Ga angle and the Ga-Cl bond length. The topological charge density analysis of LL³ demonstrates that there is no Ga-Ga bonding in Ga₂H₆, and this should also be the case for Ga₂Cl₂H₄. The range in angles is 91.3–92.0°, except for the 96.0° from the crude 3-21G-optimized geometry. The obvious conclusion is that the basis set will make little difference in the predicted angle. The primary source of error in the ab initio Ga-Ga nonbonded distance is due to the theoretical Ga-Cl bond length.

The effects of electron correlation evaluated with the 3-21G* basis set are given in Table II. Electron correlation shortens the Ga-Cl distance considerably: 0.039 Å for MP2 and 0.028 Å for CISD. Since MP2 frequently overestimates correlation effects, the limit for the 3-21G* basis set is probably between the MP2 and CISD values. The difference between the TZ2P+f SCF Ga-Cl bond length of 2.393 Å and the experimental distance of 2.349 Å could well be accounted for by electron correlation effects (~0.035 Å) and further improvements in the basis set. It should be noted here that the Ga-Cl distance is distinct and should be an easily identified peak in the electron diffraction data and that the latter should be more reliable than theory.

The effect of larger basis sets and electron correlation on the Ga-Cl bond can be examined for the diatomic molecule GaCl, which has ¹Σ⁺ ground state and an r_e of 2.2017 Å.²¹ The lack of polarization functions in the 3-21G SCF and ECP-DZ computations give rise to bond lengths which are too long, 2.308 and 2.293 Å, respectively. The addition of one set of polarization d functions improves the Ga-Cl distance to 2.255 and 2.217 Å for 3-21G* SCF and ECP-DZP, respectively. The TZ2P+f SCF Ga-Cl length of 2.228 Å shows considerable improvement over the 3-21G* SCF; The DZP SCF Ga-Cl distance in ¹Σ⁺ GaCl is 2.236 Å, showing that much of the difference is due to inadequacies in the 3-21G basis. Electron correlation effects are estimated by using both the 3-21G* SCF and TZ2P+f bases. With the 3-21G* basis, MP2 reduces the bond length by 0.033 Å whereas CISD predicts a bond distance only 0.026 Å shorter than SCF. The TZ2P+f differences are similar, with MP2 predicting a bond 0.035 Å shorter than SCF and CISD having an optimum distance 0.022 Å shorter than SCF in the TZ2P+f basis. Taking the TZ2P+f SCF distance and estimating the electron correlation contribution from 3-21G* CISD leads to a predicted bond distance of 2.2016 Å, only 0.0001 Å different from experiment and in good agreement with the TZ2P+f CISD value of 2.206 Å. Application of this simple procedure to Ga₂Cl₂H₄ results in a Ga-Cl_b distance of 2.365 Å, which is fairly close to the experimental r₀ of 2.349 Å, considering the approximations made here.

The theoretical and experimental nonbonded Ga-Ga distances cannot be reconciled even with use of the experimental Ga-Cl distance, due to the difference in the interior ring angles. The experimental value for the Ga-Cl_b-Ga angle is 87.2°, whereas we predict the theoretical angle to be within 2° of 90°, after taking into account correlation and basis set effects. The experimental Ga-Ga distance peak in the radial distribution curve is in the range where Cl-Cl and Cl-H distances are expected to appear, making determination of the Ga-Cl-Ga angle from electron diffraction less clear-cut.

There is little question about the final two structural parameters. The H-Ga-H angle, which could not be determined from the

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Table III. SCF Harmonic Vibrational Frequencies for $\text{Ga}_2\text{Cl}_2\text{H}_4$ (cm^{-1})

	3-21G*	HUZ-SV**	DZP
a_g	144	147	146
	306	304	289
	767	785	781
	2056	2076	2130
b_{1g}	180	173	152
	669	684	688
b_{2g}	471	478	482
	2052	2075	2124
b_{3g}	465	476	470
	466	477	470
a_u	31	28	39
b_{1u}	496	502	505
	2055	2079	2127
b_{2u}	285	286	266
	719	734	738
b_{3u}	281	276	265
	745	768	763
	2052	2072	2126

electron diffraction data and was fixed⁵ at 120° , is predicted to be within 1° of 132° on the basis of the results given in Tables I and II. The experimental Ga–H bond length of 1.559 Å is consistent with the TZ2P+f SCF value of 1.553 Å and the effect of correlation to lengthen the Ga–H bond by ~ 0.007 Å.

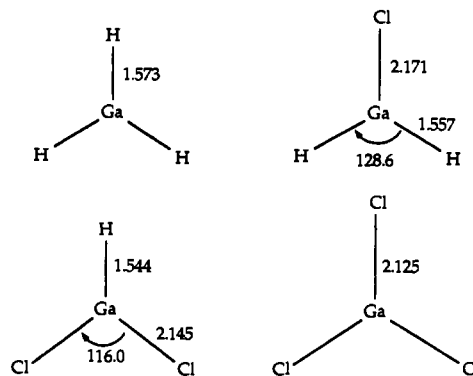
The performance of the less rigorous ECP methods is similar to that for the all-electron methods. Polarization functions on gallium lead to marked reductions in the size of the bridge region, but not sufficient to agree with experiment. ECP methods may sometimes be useful in their own right. The particular ECP-DZP basis we utilized gave results for the four-membered ring which are fortuitously somewhat closer to the experimental results than the best *ab initio* basis sets, but are inferior for the terminal bonds. This is borne out by the error in the Ga–Cl distance of 0.022 Å for ECP-DZP SCF, in contrast to the Ga–H error of -0.022 Å! ECP methods are likely to be the only feasible ones for much larger molecules containing gallium in the near future. However, these methods would clearly benefit from methodological advances.

The conclusion is that while the terminal bonds are well represented at the levels of theory used in this study, the four-membered ring is more problematic. All methods considered predict the bridge bonds to be longer than experiment. Extending the basis set beyond DZP gives significant reductions in the Ga–Cl bond distance. Inclusion of electron correlation is clearly important, but it is not currently feasible to include these effects in a proper manner, i.e. in conjunction with a large basis set including *f* functions. The *f* functions are more important for $\text{Ga}_2\text{Cl}_2\text{H}_4$ than for Ga_2H_6 because Cl polarizes the occupied *d* electrons of Ga more than H does. However, the problems in regard to bond lengths notwithstanding, the predicted angles of 132 and 90° should be reliable to within 2° .

Harmonic Vibrational Frequencies for the Monochlorogallane Dimer. Harmonic vibrational frequencies with various basis sets are reported in Table III. The b_{1u} band at 33 cm^{-1} predicted by LL is described by them as IR inactive, whereas we find a very low predicted intensity. The IR band around 30 cm^{-1} is too low in both frequency and intensity to have been observed to date. Therefore one of the eight experimental bands reported earlier by Goode et al.⁵ does not appear to be a fundamental band. Recent experimental work by Downs and co-workers²² gives a much more detailed assignment of the IR bands and also the Raman bands. Theoretical predictions of the harmonic vibrational frequencies are compared with these new experimental results in Table IV for both $\text{Ga}_2\text{Cl}_2\text{H}_4$ and $\text{Ga}_2\text{Cl}_2\text{D}_4$. The agreement with experiment for many bands is reasonable and comparable to that found in other studies. In view of the gap between the *ab initio* predictions and experiment on the bridge geometry, it might be expected that concomitant differences would be found for vibrations predominantly in the four-membered ring. These vi-

Table IV. Harmonic Vibrational Frequencies (cm^{-1}), Comparison of Theory (DZP SCF) and Experiment,^{5,22} and Assignment of IR Bands for $\text{Ga}_2\text{Cl}_2\text{H}_4$ and $\text{Ga}_2\text{Cl}_2\text{D}_4$ (DZP SCF Predictions of IR Intensities in Parentheses)

	$\text{Ga}_2\text{Cl}_2\text{H}_4$		$\text{Ga}_2\text{Cl}_2\text{D}_4$		assgnt
	theory	expt	theory	expt	
a_g	2130	1990	1509	1425	Ga–H str
	781	690	558	490	GaH ₂ scissor
	289	250	289	245	Ga–Cl str
b_{1g}	146	120	144	120	ring def
	688	575	498	420	GaH ₂ rock
	152	295	151	285	Ga–Cl str
b_{2g}	2124	2020	1517	1455	Ga–H str
	482	472	347	345	GaH ₂ wag
b_{3g}	470	510	338	375	GaH ₂ twist
	470		333		GaH ₂ twist
a_u	2127 (416)	2020	1520 (214)	1450	Ga–H str
b_{1u}	505 (38)	480	373 (23)	355	GaH ₂ wag
	39 (3)		38 (2)		ring pucker
b_{2u}	738 (369)	578	529 (203)	410	GaH ₂ rock
	266 (60)	290	265 (53)	305	Ga–Cl str
b_{3u}	2126 (96)	1985	1506 (52)	1420	Ga–H str
	764 (493)	690	544 (237)	495	GaH ₂ scissor
	265 (159)	265	265 (156)	265	Ga–Cl str

**Figure 1.** DZP SCF predicted geometries of the monomers, GaH_3 , GaClH_2 , GaCl_2H , and GaCl_3 . Bond distances are in angstroms and bond angles in degrees.

brations are readily identified as those with a small or zero change in frequency upon deuteration.

The largest discrepancy is indeed for the b_{1g} vibration (Ga–Cl stretch) of 295 cm^{-1} , which is severely underestimated as 153 cm^{-1} by the theory. The IR-active ring vibrations involving Ga–Cl stretching are predicted at 266 and 265 cm^{-1} , in contrast to the experimental $\text{Ga}_2\text{Cl}_2\text{H}_4$ fundamentals of 290 and 265 cm^{-1} . Most of the remaining experimental fundamentals agree well with theory, recalling that SCF frequencies are up to 10% too high, as found in many other studies. The assignments of modes with large isotope shifts to vibrations involving significant motions of H nuclei are supported by our predicted isotope shifts. However, the SCF frequencies for the Raman-active GaH_2 twist at 470 cm^{-1} (experiment 510 cm^{-1}) and the IR-active GaH_2 rock at 738 cm^{-1} (experiment 578 cm^{-1}) are outside this norm. It seems likely that a more accurate geometry, particularly for the bridge region, is required before more reliable harmonic frequencies can be obtained by theory. Anharmonic effects could conceivably be important as well, but these cannot be predicted at present by *ab initio* theory for molecules as large as $\text{Ga}_2\text{Cl}_2\text{H}_4$.

Isomers of $\text{Ga}_2\text{Cl}_2\text{H}_4$ and $\text{Ga}_2\text{Cl}_2\text{D}_4$ and Dissociation Energies. The monomers GaClH_2 , GaCl_2H , and GaCl_3 have been investigated at the SCF level with the DZP basis set. The optimized geometries are shown in Figure 1. The Ga–Cl bond distance decreases with increasing substitution by chlorine, similar to the well-known reduction of carbon–halogen bond distances with increasing halogen substitution.

The monochlorogallane dimer structure with two chlorine atoms in the bridge region (I) is one of five possible isomers of $\text{Ga}_2\text{Cl}_2\text{H}_4$. These five isomers are shown in Figure 2 along with the fully optimized DZP SCF geometrical parameters. With terminal

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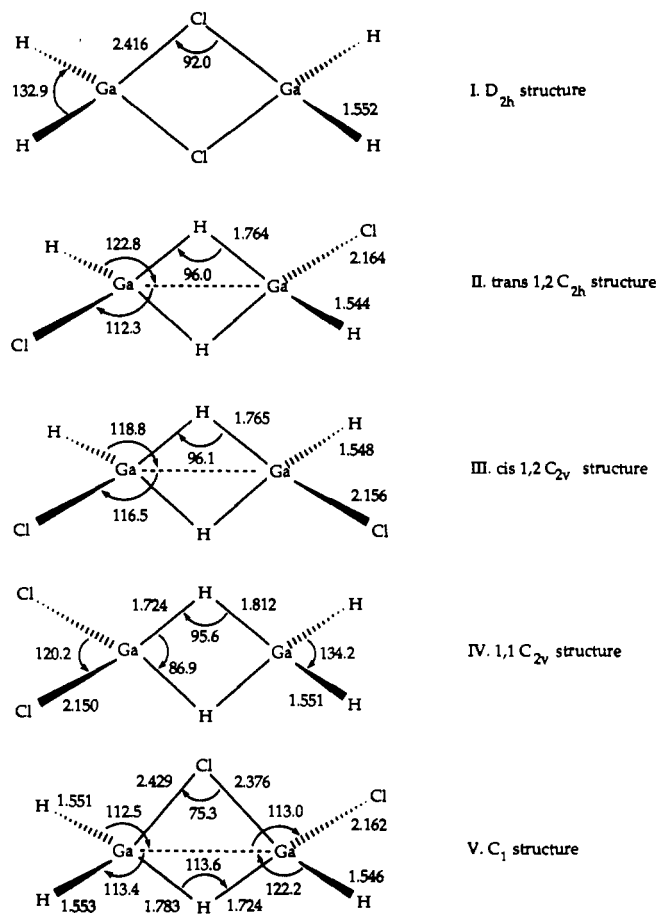


Figure 2. DZP SCF predicted geometries of the isomers of $\text{Ga}_2\text{Cl}_2\text{H}_4$. Bond distances are in angstroms and bond angles in degrees. Additional geometry information is as follows. III: $\tau(\text{Ga}-\text{H}_b-\text{Ga}-\text{H}_b) = -1.3$. V: $\angle\text{Cl}_b-\text{Ga}(\text{GaClH})-\text{H}_b = 87.0$, $\angle\text{Cl}_b-\text{Ga}(\text{GaH}_2)-\text{H}_b = 84.1$, $\angle\text{Cl}_b-\text{Ga}-\text{Cl}_t = 108.8$, $\tau(\text{H}_t-\text{Ga}-\text{Ga}-\text{H}_t) = -0.4$, $\tau(\text{H}_t-\text{Ga}-\text{Ga}-\text{H}_t) = -171.6$, $\tau(\text{H}_t-\text{Ga}-\text{Ga}-\text{Cl}_t) = 169.3$; ring torsions (anticlockwise), $\tau(\text{Ga}-\text{Cl}_b-\text{Ga}-\text{H}_b) = 1.3$, $\tau(\text{Cl}_b-\text{Ga}-\text{H}_b-\text{Ga}) = -1.8$, $\tau(\text{Ga}-\text{H}_b-\text{Ga}-\text{Cl}_b) = 1.9$, $\tau(\text{H}_b-\text{Ga}-\text{Cl}_b-\text{Ga}) = -1.3$.

chlorine atoms on each gallium atom, there are trans- (C_{2h}) (II) and cis-1,2 (C_{2v}) (III) isomers. With two terminal chlorine atoms on the same gallium atom, the 1,1 isomer (C_{2v}) (IV) is obtained. This is the only isomer that would not be expected to dissociate into two monochlorogallane monomer units or be formed from their association. Finally, there is the totally asymmetric (C_1) structure (V) with one bridging and one terminal chlorine. The same trends seen in the monomer bond lengths are also present in the dimers. In structure IV of Figure 2, the difference between the $\text{Ga}-\text{H}_b$ bond distances is 0.088 Å, with the shorter bond to the chlorinated Ga. Structure V also exhibits differences of 0.052 and 0.062 Å in the $\text{Ga}-\text{Cl}_b$ and $\text{Ga}-\text{H}_b$ bond distances, respectively. The influence of neighboring bonds seems more pronounced if the neighboring bond being considered is a terminal bond rather than a bridging bond.

Energies at the DZP SCF level are shown in Table V and compared with the energy of two monomer units. All five isomers of the monochlorogallane dimer are stable at this level of theory with respect to two monomers. Isomer IV however would be expected to dissociate into gallane and dichlorogallane, rather than two monochlorogallanes. For this process, the dissociation energy is 10.2 kcal mol⁻¹ instead of 7.0 kcal mol⁻¹. The SCF dissociation energies will be less than the experimental ones (see below). Bridging through chlorine atoms is favored over bridging via hydrogen atoms by approximately 7 kcal mol⁻¹ per Cl atom. Chlorine atoms on the two terminal positions very slightly prefer being trans rather than cis to each other, presumably due to a small repulsion between the negatively charged Cl atoms. The SCF binding energy of the most stable D_{2h} isomer is predicted to be 21 kcal mol⁻¹, less than the 26 kcal mol⁻¹ predicted by LL⁸

Table V. DZP SCF Energies for Isomers of $\text{Ga}_2\text{Cl}_2\text{H}_4$ and $\text{Ga}_2\text{Cl}_4\text{H}_2$ ^a

isomer	$\text{Ga}_2\text{Cl}_2\text{H}_4$		$\text{Ga}_2\text{Cl}_4\text{H}_2$	
	au	kcal mol ⁻¹	au	kcal mol ⁻¹
D_{2h}	-4767.605 352	0.0	-5685.496 780	18.5
trans-1,2 (C_{2h})	-4767.585 021	12.8	-5685.526 270	0.0
cis-1,2 (C_{2v})	-4767.583 470	13.7	-5685.525 737	0.3
1,1 (C_{2v})	-4767.583 935	13.4	-5685.524 120	1.4
C_1	-4767.594 192	7.0	-5685.511 123	9.5
two monomers	-4767.572 518	20.6	-5685.499 358	16.9

^a Energies in kcal mol⁻¹ are relative to the most stable isomer.

using the 3-21G* basis. This is consistent with their result for the binding energy of digallane, which is reduced at the SCF level upon improving the basis set, due to decreasing basis set superposition errors.

The effect of correlation on the binding energy is significant when compared to the magnitude of the overall dimerization energy. At the 3-21G* MP2 level of theory, the dissociation energy of structure I is 38 kcal mol⁻¹, whereas Davidson-corrected CISD²³ gives 36 kcal mol⁻¹ for dissociation to a supermolecular system of two monomers separated by a large distance. The use of a supermolecule is needed because of the well-known size-extensivity problem for limited CI expansions. The Davidson correction approximates the effects of quadruple substitutions, which are the most important ones unaccounted for in CISD. Without the use of a supermolecule approach for the monomers and the Davidson correction, the 3-21G* CISD dissociation energy of $\text{Ga}_2\text{Cl}_2\text{H}_4$ is 13 kcal mol⁻¹ less than the 3-21G* SCF energy, which is manifestly incorrect. When considering the Table V dissociation energies, one should keep in mind the increase in binding energy of 8–10 kcal mol⁻¹ from electron correlation effects. The correlation contribution to the dimerization energies of both Al_2H_6 and Ga_2H_6 from the work of LL³ is also 8–10 kcal mol⁻¹. The effect in diborane is quite a bit larger (at 22 kcal mol⁻¹). This difference arises from the greater extent of ionic bonding in dialane and digallane. Once electron correlation is included, the effects are more or less constant; i.e., the dimerization energies from various electron correlation methods differ by no more than 2 kcal mol⁻¹ in ref 3 or between MP2 and CISD in our work.

A relatively minor effect is zero-point vibrational energy (ZPVE), which is expected to raise the energy of the dimers because they have more vibrational modes. This is indeed seen for structure I, for which the dissociation energy decreases by 1.6 kcal mol⁻¹ when ZPVE is added. At temperatures above absolute zero, entropy effects will favor the monomers over the dimer as well.

$\text{Ga}_2\text{Cl}_4\text{H}_2$ similarly has five isomers with the role of chlorine and hydrogen atoms reversed from those in the monochlorogallane dimer. Figure 3 contains the DZP SCF optimized geometries for the five isomers. There are no experimental data on the structure of $\text{Ga}_2\text{Cl}_4\text{H}_2$, unfortunately. Examination of structure I of Figure 3 shows that the $\text{Ga}-\text{H}_b-\text{Ga}$ angle is similar to those in Figure 2. The $\text{Ga}-\text{H}$ and $\text{Ga}-\text{Cl}$ bond distances are generally smaller for $\text{Ga}_2\text{Cl}_4\text{H}_2$ than for $\text{Ga}_2\text{Cl}_2\text{H}_4$. An extreme difference of 0.121 Å in $\text{Ga}-\text{Cl}_b$ bonds in the same molecule is seen in structure IV of Figure 3, just as the largest variations in $\text{Ga}-\text{H}_b$ are both contained in structure IV of Figure 2. An important fact to note for latter discussion is that, for all of the DZP SCF geometries in Figures 2 and 3 in which two Cl atoms are bridging, the $\text{Ga}-\text{Cl}-\text{Ga}$ angle varies from 91.8 to 92.2°.

Energies for these isomers are also shown in Table V. Here the D_{2h} isomer (I) with two bridging hydrogen atoms and all four chlorine atoms in terminal positions is not expected to be the lowest energy isomer. The isomer of lowest energy is the trans-1,2 isomer (II), although the cis-1,2 (III) and 1,1 isomers (IV) are only slightly higher in energy. The latter would dissociate into mo-

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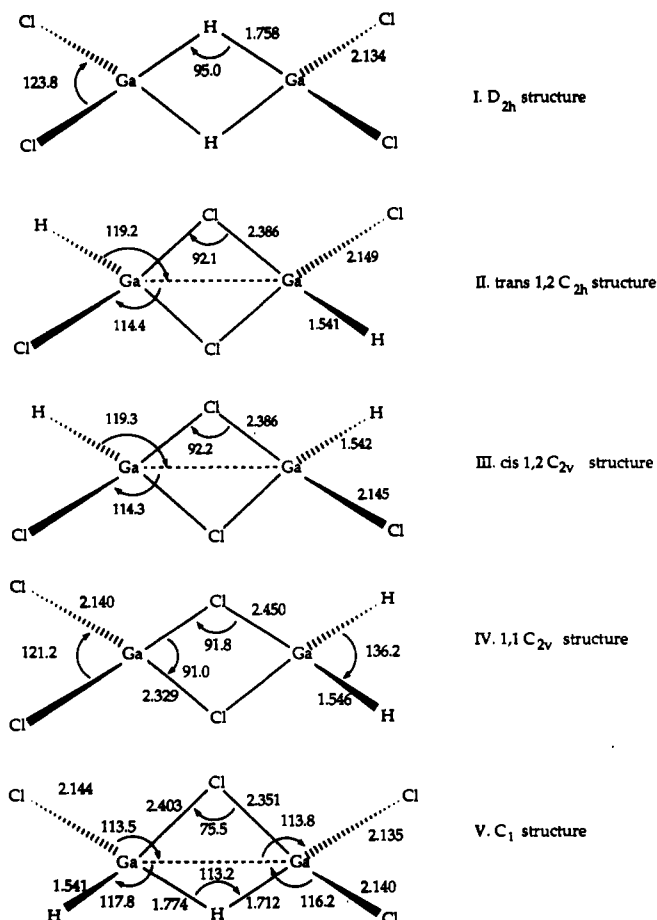


Figure 3. DZP SCF predicted geometries of the isomers of $\text{Ga}_2\text{Cl}_2\text{H}_4$. Bond distances are in angstroms and bond angles in degrees. Additional geometry information is as follows. III: $\tau(\text{Ga}-\text{Cl}_b-\text{Ga}-\text{Cl}_b) = 1.4$. V: $\angle\text{Cl}_b-\text{Ga}(\text{GaClH})-\text{H}_b = 84.2$, $\angle\text{Cl}_b-\text{Ga}(\text{GaCl}_2)-\text{H}_b = 87.1$, $\angle\text{H}_b-\text{Ga}-\text{H}_t = 113.4$, $\tau(\text{Cl}_t-\text{Ga}-\text{Ga}-\text{Cl}_t) = -0.4$, $\tau(\text{Cl}_t-\text{Ga}-\text{Ga}-\text{H}_t) = -190.7$, $\tau(\text{Cl}_t-\text{Ga}-\text{Ga}-\text{Cl}_t) = 167.6$; ring torsions (anticlockwise), $\tau(\text{Ga}-\text{Cl}_b-\text{Ga}-\text{H}_b) = 1.0$, $\tau(\text{Cl}_b-\text{Ga}-\text{H}_b-\text{Ga}) = -1.4$, $\tau(\text{Ga}-\text{H}_b-\text{Ga}-\text{Cl}_b) = 1.4$, $\tau(\text{H}_b-\text{Ga}-\text{Cl}_b-\text{Ga}) = -1.0$.

Table VI. DZP SCF Equilibrium Geometries for Ga_2Cl_6 (Distances, Å; Angles, deg)

basis	$R(\text{Ga}-\text{Ga})$	$R(\text{Ga}-\text{Cl}_b)$	$R(\text{Ga}-\text{Cl}_t)$	$\angle\text{Cl}_t-\text{Ga}-\text{Cl}_t$
DZ	3.570	2.411	2.159	124.2
DZP	3.385	2.358	2.129	123.6
ECP-DZ	3.524	2.385	2.133	125.8
ECP-DZP	3.308	2.316	2.098	123.1
expt ²⁴	3.301	2.300	2.099	124.6

nochlorogallane and gallium trichloride, which it lies below by $16.5 \text{ kcal mol}^{-1}$ at the SCF level. Chlorine bridging is favored over hydrogen bridging by over 9 kcal mol^{-1} , slightly more than in the case of the monochlorogallane dimers. The isomer of highest energy (isomer I in Figure 3) lies above the monomer dissociation limit at the SCF level of theory. Once electron correlation is added, it should be weakly bound, with the terminal Cl atoms withdrawing electron density from the bridge bonds.

The structural trends in the isomers of both the monochlorogallanes and the dichlorogallanes are probably correct, although the four-membered ring is predicted to be too large, as with the known isomer of the monochlorogallane dimer.

The gallium trichloride dimer is the largest system studied here. Results obtained by using various basis sets and methods are presented in Table VI. Again, the size of the four-membered ring is overestimated when compared to experiment.²⁴ (Reference

25 gives a crystal structure for Ga_2Cl_6 with lower resolution.) Inclusion of polarization functions is clearly important, giving a significant reduction of the Ga-Ga and Ga-Cl_b distances. However, the DZP SCF geometry predictions are closer to experiment for Ga_2Cl_6 than for $\text{Ga}_2\text{Cl}_2\text{H}_4$. The difference in the DZP SCF Ga-Cl_b distance is 0.058 Å , contrasted to 0.067 Å for $\text{Ga}_2\text{Cl}_2\text{H}_4$. Also, the DZP SCF Ga-Cl-Ga angle of 91.7° agrees exactly with the experimental value. Given the constancy of the Ga-Cl-Ga angle in the dibridged systems at the DZP SCF level, it is difficult to imagine that the interior angle in question is 87.2° in $\text{Ga}_2\text{Cl}_2\text{H}_4$ as suggested by experiment. The ECP-DZP result is in remarkable agreement with experiment, probably due to a cancellation of errors, with the effective core potential underestimating the bond lengths and the inadequacies of the basis set increasing the bond lengths.

The dimerization energy of gallium trichloride at the DZP SCF level is $9.7 \text{ kcal mol}^{-1}$, comparable to those of the mono- and dichlorogallanes at the same level of theory. Again, we note that the dimerization energies predicted at this level of theory are expected to be $5\text{--}10 \text{ kcal mol}^{-1}$ less than the experimental values. The binding energy of the dimers increases by $6\text{--}8 \text{ kcal mol}^{-1}$ if a Cl atom appears in a bridging position in place of a H atom and decreases by $1\text{--}2 \text{ kcal mol}^{-1}$ per Cl substitution on the terminal bonds. Bridging through the chlorine atoms is preferred, as Cl has extra valence electrons, and Lewis dot structures can be drawn, diminishing the necessity of invoking the three-center, two-electron bond.

Conclusions

The nonbonded Ga-Ga distance may be thought of as dependent on the Ga-Cl_b bond length and the Ga-Cl-Ga angle. The source of disagreement between ab initio theory and experiment for $\text{Ga}_2\text{Cl}_2\text{H}_4$ is thus due to the difficulty theory has in obtaining an accurate Ga-Cl_b distance (which requires a TZ2P+f basis set with a correlated method) and the likely underestimation of the Ga-Cl-Ga angle from electron diffraction data. The H-Ga-H angle, which was arbitrarily fixed at 120° in the ED refinement, is predicted here to be 132° . The Ga-Cl-Ga angle is predicted here to be 90° (rather than the experimental value of 87.2°). These angles should be accurate within 2° . The agreement of ab initio results with Ga_2Cl_6 experimental values is better for the bond angles. With increasing Cl substitution on Ga, particularly substitution at nonbridging sites, neighboring bonds become shorter.

The stabilities of the dimers decrease with increasing chlorination of terminal Ga-X bonds by $1\text{--}2 \text{ kcal mol}^{-1}$ per Cl substitution and increase by $6\text{--}8 \text{ kcal mol}^{-1}$ with each chlorine substitution for bridging H atoms. Thus the chlorine-bridged dimer of monochlorogallane has the largest association energy. After electron correlation and zero-point vibrational energy are taken into account, each of the dimers considered will probably be bound, although some very weakly so. The theoretical and experimental vibrational spectra agree well, except for ring vibrational modes that are predicted to be too low because of the overestimation of the spatial extent of the bridge region at the DZP SCF level.

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Registry No. I- $\text{Cl}_2\text{Ga}_2\text{H}_4$, 119414-01-6; I- $\text{Cl}_4\text{Ga}_2\text{H}_2$, 136184-91-3; II- $\text{Cl}_2\text{Ga}_2\text{H}_4$, 136184-88-8; II- $\text{Cl}_4\text{Ga}_2\text{H}_2$, 136235-65-9; III- $\text{Cl}_2\text{Ga}_2\text{H}_4$, 136235-64-8; III- $\text{Cl}_4\text{Ga}_2\text{H}_2$, 136235-66-0; IV- $\text{Cl}_2\text{Ga}_2\text{H}_4$, 136184-89-9; IV- $\text{Cl}_4\text{Ga}_2\text{H}_2$, 136184-92-4; V- $\text{Cl}_2\text{Ga}_2\text{H}_4$, 136184-90-2; V- $\text{Cl}_4\text{Ga}_2\text{H}_2$, 136184-93-5; Cl_6Ga_2 , 15654-66-7; D_2 , 7782-39-0; ClGaH_2 , 43311-11-1; Cl_2GaH , 13886-65-2; Cl_3Ga , 13450-90-3; gallium hydride, 131641-96-8.

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