An *Ab Initio* Study on Dichlorodigallane, $Ga_2Cl_2H_4$

Koop Lammertsma* and Jerzy Leszczyński

Department of Chemistry, University of Alabama at Birmingham, UAB Station 219 PBS, Birmingham, Alabama 35294, U.S.A.

Geometrical parameters and vibrational frequency data for the dimer of monochlorogallane obtained by *ab initio* calculations show excellent agreement with experimental values; the dissociation energy of $Ga_2Cl_2H_4$ to the $GaClH_2$ monomers and GaCl + H_2 has been calculated.

The heavier atom analogues of diborane(6) are of both experimental and theoretical interest. Most halogeno derivatives have been characterized for the dimers of B, Al, Ga, and In.[1] However, little information is available for the hydrido forms and this is limited in the case of digallanes to the tetrahalogeno derivative $Ga_2H_2X_4$ (X = Br, Cl) and the methylated species $Ga_2H_2Me_4$.[2] As for Ga_2Cl_4 and In_2Cl_4,[3] dialane(4)[4] also has ionic character, in contrast to diborane(4).[5] Theoretical studies on gallium compounds have been hampered by the high cost of *ab initio* calculations, which require at least a split valence basis set with added d-type functions (HF/3-21G*).[6] Recently, GaCl, GaH, and GaH_3 were studied at this level of theory[6] but for the bi- and tri-dentate forms of the mixed boron–gallium hydride $GaBH_6$ pseudopotentials were used.[7]

Here we present an *ab initio* study and frequency analysis on the dichlorodigallane(6), $H_2Ga\text{-}\mu Cl_2\text{-}GaH_2$. Recently, Goode *et al.*[8] reported the gas-phase electron diffraction data and vibrational spectra for this compound, that was first prepared by Greenwood and Storr.[9] We wanted to verify the experimental finding and calculate the dimerization energy using the 3-21G* basis set that has d-type valence functions for both gallium and chlorine.

Structure (**1**) was optimized[10] within D_{2h} symmetry using GAMESS.[11] The calculated (HF/3-21G*) and experimental (in parentheses) molecular parameters for (**1**) are shown in Figure 1. The harmonic vibrational frequencies of the optimized geometry were obtained from diagonalization of the force constant matrix at the same level of theory. Since all eigenvalues of the Hessian matrix of (**1**) are positive it is a

Table 1. Vibrational frequencies (cm^{-1}) and i.r. intensities (debye^2/a.m.u. Å^2) for gallium structures.

$Ga_2Cl_2H_4$			$GaClH_2$	GaCl
Calc.	Exp.	Type	Calc.	Calc.
278 (4.5)	265 (s)	Ga_2Cl_2 (a)sym. str.	413 (1.8)	358 (2.8)
281 (1.7)	290 (wsh)	Ga_2Cl_2 asym. str.		
458 (2.9)	382 (m)	Ga_2H_2 twist		
501 (1.9)	480 (mw)	Ga_2H_2 rock	526 (1.3)	
720 (6.6)	575 (m)	Ga_2H_2 wag	634 (3.8)	
756 (9.9)	678 (vs)	GaH_2 bend	788 (4.8)	
2034 (3.6)	1990 (sh)	GaH_2 sym. str.	2032 (5.1)	
2036 (10.3)	2020 (s)	GaH_2 asym. str.	2037 (1.5)	

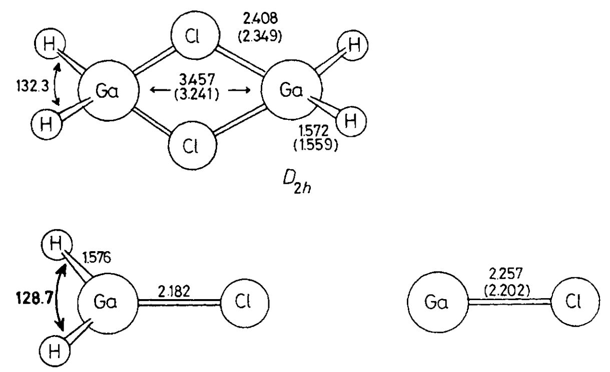

Figure 1. Calculated (3-21G*) $Ga_2Cl_2H_4$, $GaClH_2$, and GaCl structures. The experimental values for $Ga_2Cl_2H_4$ (ref. 8) and GaCl (ref. 12) are given in parentheses.

minimum energy structure. Table 1 gives the calculated i.r. active frequencies and intensities† together with Goode's experimental data. Table 1 also lists the calculated data for the fragment molecules $GaClH_2$ (C_{2v}) and GaCl.

The calculated and experimental molecular parameters are in good agreement, although the 3-21G* separation between the two galliums of 3.457 Å is longer than the observed value by 0.216 Å, which reflects a 6.7% difference. This may not be surprising because the Ga–Ga interaction is at best weak. For comparison, the experimental Ga–Ga separations in μ-dichloro-tetramethyldigallane and Ga_2Cl_6 are 3.328 and 3.301 Å respectively, with a much shorter distance of 2.610 Å for the μ-hydrido $Ga_2H_2Me_4$. The difference in the calculated and experimental bridging Ga–Cl bonds of (**1**) amounts to only 0.059 Å or 2.5%. As expected, this Ga–Cl bond is longer (0.226 Å) than in the $GaClH_2$ monomer. The Ga–H bond lengths are virtually the same with only a marginal difference (0.80%) from the experimental value.

The vibrational frequencies and intensities show good agreement with the experimental values, considering that the latter were obtained on a solid film at 77 K. The two lowest i.r. frequencies of 278 (B_{3u}) and 281 cm^{-1} (B_{1u}) are the characteristic vibrational modes for the dimer (**1**).

We also investigated the binding energy of (**1**) with respect to its $GaClH_2$ monomer as well as its decomposition to GaCl and a hydrogen molecule, which is reported to occur at room temperature. From the total 3-21G* energies, *i.e.* −4745.26845 a.u. for (**1**), −2372.61313 a.u. for $GaClH_2$, −2371.48548 a.u. for GaCl, and −1.12296, for H_2, a monochlorogallane dimerization energy of 26.5 kcal/mol (1 cal = 4.184 J) is calculated. The dissociation of $GaClH_2$ to GaCl and hydrogen is endothermic by only 2.9 kcal/mol. When zero-point energy corrections are included these binding energies decrease to 24.6 and 0.9 kcal/mol, respectively. Inclusion of the effects of electron correlation are expected to increase these values. However, such calculations were beyond our means.

In conclusion, *ab initio* theory at the 3-21G* level satisfactorily describes the structure and vibrational frequencies of the monochlorogallane dimer $Ga_2Cl_2H_4$ and appears in good agreement with the recent experimental data of Goode *et al.*[8] Studies on gallium hydrides are in progress.

We acknowledge the Alabama Supercomputer Network for the generous allotment of computer time.

Received, 7th February 1989; Com. 9/00605B

References

1 K. Wade and A. J. Banister, 'The Chemistry of Aluminium, Indium and Thallium,' Pergamon, Oxford, 1975; F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Wiley, New York, 1980.
2 N. N. Greenwood, in 'New Pathways in Inorganic Chemistry,' eds. E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Cambridge University Press, 1968.
3 P. L. Randloff and G. N. Papatheodorou, *J. Chem. Phys.*, 1980, **72**, 992.
4 K. Lammertsma, O. F. Güner, R. M. Drewes, A. E. Reed, and P. v. R. Schleyer, *Inorg. Chem.*, 1989, **28**, 313.
5 R. R. Mohr and W. N. Lipscomb, *Inorg. Chem.*, 1986, **25**, 1053.
6 K. D. Dobbs and W. J. Hehre, *J. Comput. Chem.*, 1986, **7**, 359.
7 V. Barone, C. Minichino, F. Lelj, and N. Russo, *J. Comput. Chem.*, 1988, **9**, 518.
8 M. J. Goode, A. J. Downs, C. R. Pulham, D. W. H. Rankin, and H. E. Robertson, *J. Chem. Soc., Chem. Commun.*, 1988, 768.
9 N. N. Greenwood and A. Storr, *J. Chem. Soc.*, 1965, 3426.
10 For an introduction to the methods employed, see: W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, 'Ab Initio Molecular Orbital Theory,' Wiley, New York, 1986.
11 GAMESS: M. Dupuis, D. Spangler, J. J. Wendolski, NRCC Software Catalog, University of California: Berkeley, CA, 1980, Program QG01; M. W. Schmidt, J. A. Boatz, K. K. Baldridge, S. Kosecki, M. S. Gordon, S. T. Elbert, and B. Lam, *QCPE Bulletin*, 1987, **7**, 115.
12 J. H. Callomon, E. Hirota, K. Kuchitsu, W. J. Latterty, A. G. Maki, and C. S. Pote, 'Structure Data on Free Polyatomic Molecules,' Landolt-Bornstein, New Series, Group II, Springer-Verlag, Berlin, 1976, vol. 7.

---

† The other computed frequencies with zero i.r. intensities are: 33, 141, 169, 300, 458, 476, 662, 776, 2034, and 2038 cm^{-1}.