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Inductive effects on bridging Ga–Cl distances: the molecular structure of the dichloro(methyl)gallium dimer, $[Me_2Cl_2Ga_2(\mu\text{-}Cl)_2]$, determined by gas electron diffraction

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Abstract

The gas-phase electron diffraction data for $[Me_2Cl_2Ga_2(\mu\text{-}Cl)_2]$ are consistent with a *trans* model of C_{2h} symmetry and bond distances (r_a) Ga–C = 194.9(7) pm, Ga–Cl_t = 212.9(3) pm and Ga–Cl_b = 233.9(3) pm.

Key words: Gallium; Chlorine; Electron diffraction

1. Introduction

The molecular structures of the chlorine-bridged dimers $[X_4Ga_2(\mu\text{-}Cl)_2]$ ($X = CH_3$ or Cl) have been determined previously by gas-phase electron diffraction [1,2]. The bridging Ga–Cl bond distances are 237.8(4) pm when $X = Me = CH_3$, and 230.0(1) pm when X = Cl. We report here the structure of the intermediate compound $[Me_2Cl_2Ga_2(\mu\text{-}Cl)_2]$.

The complex $[Me_2Cl_2Ga_2(\mu\text{-}Cl)_2]$ may adopt conformations with terminal Cl atoms at the same side (*cis*) or at opposite sides (*trans*) of the central $Ga_2(\mu\text{-}Cl)_2$ ring plane. Recent SCF MO calculations on this molecule [3] as well as on the H analogue $[H_2Cl_2Ga_2(\mu\text{-}Cl)_2]$ [4] suggest that the *trans* conformer is the more stable, but that the energy of the *cis* conformer is less than 4 kJ mol^{-1} higher. The ^1H NMR [5] spectrum at ambient temperature, however, contains only one sharp line, showing that only one of the two conformers is present in detectable quantities. Moreover, Raman [6] and IR [6] spectra of $[Me_2Cl_2Ga_2(\mu\text{-}Cl)_2]$ contain the number of lines and exhibit the mutual exclusion of lines expected for the centrally symmetric *trans* isomer.

2. Results and discussion

The complex $[Me_2Cl_2Ga_2(\mu\text{-}Cl)_2]$ was prepared from $SiMe_4$ and $GaCl_3$ [6] and characterized by IR spectra [6] and elemental analysis for Cl, C and H. Gas-phase electron diffraction data were recorded in Oslo on a Balzers Eldigraph KDG-2 [7] with a nozzle temperature of 84 ± 5°C. Structural refinements were based on six plates obtained with a nozzle-to-plate distance of 50 cm (s from 25.00 to 155.00 nm^{-1} with an increment $\delta s = 1.25$ nm^{-1}) and six plates obtained with a nozzle-to-plate distance of 25 cm (s from 37.50 to 302.50 with an increment $\delta s = 2.50$ nm^{-1}). Optical densities were recorded on the Snoopy densitometer and processed by standard procedures [8]. Atomic scattering factors were taken from Ref. 9. The resulting

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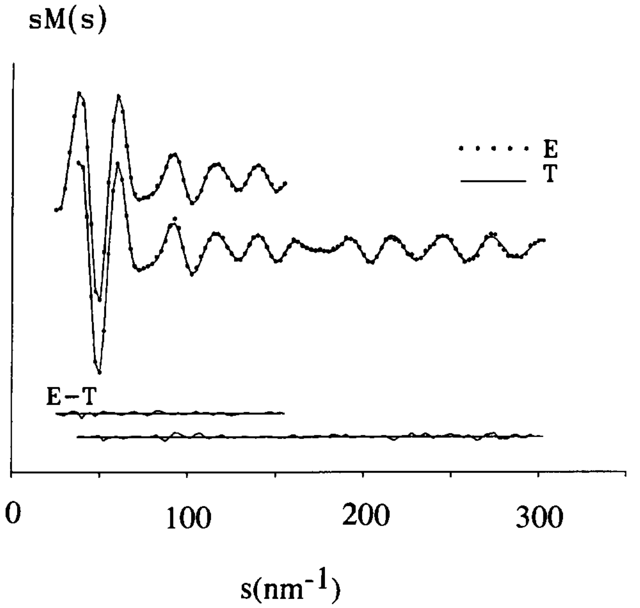

Fig. 1. Experimental (······) and calculated (———) modified molecular intensity curves for $[Me_2Cl_2Ga_2(\mu\text{-}Cl)_2]$.

modified molecular intensity curves are shown in Fig. 1. Structural analysis was carried out at the University of Moscow.

A molecular model of the *trans* form of $[Me_2Cl_2Ga_2(\mu\text{-}Cl)_2]$ is shown in Fig. 2. The molecular point group was assumed to be C_{2h}, the $GaCH_3$ fragments were assumed to have C_{3v} symmetry and methyl groups were fixed in the staggered conformation indicated in Fig. 2. The structure is then described by four bond distances: C–H, Ga–C, Ga–Cl_t (t = terminal) and Ga–Cl_b (b = bridge) and the four valence angles ∡$GaCl_bGa$, ∡Cl_bGaCl_t, ∡Cl_bGaC and ∡GaCH.

These structure parameters were refined by least squares calculations on the intensity data under the constraints of a geometrically consistent r_a structure. Vibrational amplitudes were transferred from the more symmetrical compounds $[(CH_3)_4Ga_2(\mu\text{-}Cl)_2]$ and $[Cl_4Ga_2(\mu\text{-}Cl)_2]$ [1,2]. The best values obtained for the structure parameters are listed in Table 1. The estimated standard deviations listed in the table have been multiplied by a factor of 2 to compensate for the added uncertainty due to data correlation and non-refined

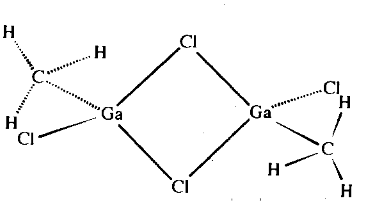

Fig. 2. Molecular model of $[Me_2Cl_2Ga_2(\mu\text{-}Cl)_2]$, point group C_{2h}.

TABLE 1. Interatomic distances (r_a), root mean square vibrational amplitudes (l) and valence angles in $[(CH_3)_2Cl_2Ga_2(\mu\text{-}Cl)_2]$ [a]

	r_a	l
Bond distances		
C–H	111(2)	9.0(13)
Ga–C	194.9(7)	5.5(2) [b]
Ga–Cl_t	212.9(3)	5.6(2) [b]
Ga–Cl_b	233.9(3)	8.5(2)
Non-bonded distances		
Ga···Ga	329.7(15)	10.7(4) [c]
Cl_b···Cl_b	331.8(17)	9.1(4) [c]
Cl_b···C	348(3)	12.1(6) [d]
Cl_b···Cl_t	357.8(13)	12.3(6) [d]
Cl_t···C	371(2)	14.0(6) [d]
Ga···C	451(4)	32(2) [e]
Ga···Cl_t	458(3)	32(2) [e]
Cl_t···C	500(4)	32(2) [e]
C···C	611(6)	9(9)
Cl_t···Cl_t	634(3)	26(6)
Valence angles		
∡Cl_bGaCl_b		90.4(6)
∡$GaCl_bGa$		89.6(6)
∡Cl_bGaCl_t		106.3(6)
∡Cl_bGaC		108.0(13)
∡Cl_tGaC		131(3)
∡GaCH		109(2)
$R = [\Sigma w(I_{obs} - I_{calc})^2/\Sigma w I_{obs}^2]^{1/2} = 0.049$		

[a] Distances and amplitudes in pm, angles in degrees, estimated standard deviations in parentheses in units of the last digit. Cl_t = terminal Cl, Cl_b = bridging Cl.

[b,c,d,e] Sets of amplitudes which were refined with constant differences.

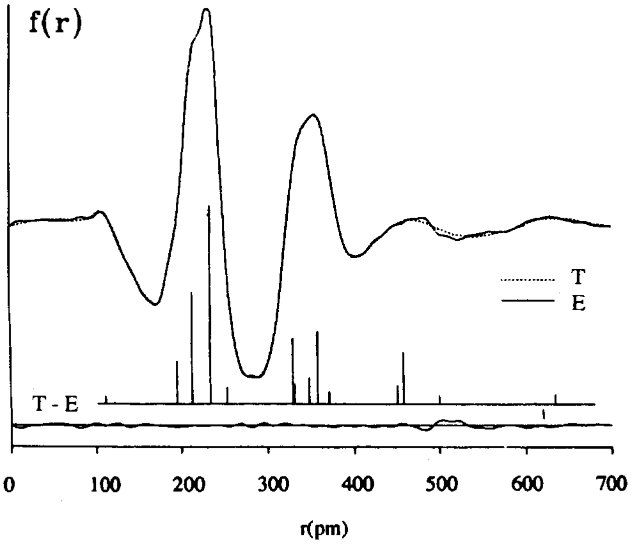

Fig. 3. Experimental (———) and calculated (······) radial distribution curve of $[Me_2Cl_2Ga_2(\mu\text{-}Cl)_2]$ obtained by Fourier inversion of experimental modified molecular intensity curves or the theoretical counterpart calculated for the best model. Major peaks are indicated by bars of height approximately proportional to the areas under the corresponding peak. Artificial damping constant $k = 20$ pm^2.

TABLE 2. Bond distances (pm) and valence angles (°) in compounds of type $[X_2Y_2Ga_2(\mu\text{-}Cl)_2]$, X, Y = Cl, H, methyl or t-butyl [a]

Compound	Ga–Cl_b	Ga–Cl_t	Ga–C	∡GaCl_bGa	∡XGaY
$Me_4Ga_2(\mu\text{-}Cl)_2$ [b]	237.8(4)		194.6(3)	88.0(9)	132(3)
$H_4Ga_2(\mu\text{-}Cl)_2$ [c]	234.9(3)		–	87.2(8)	[120]
$Me_2Cl_2Ga_2(\mu\text{-}Cl)_2$ [d]	233.9(3)	212.9(3)	194.9(7)	89.6(6)	131(3)
$Cl_4Ga_2(\mu\text{-}Cl)_2$ [e]	230.0(1)	209.9(1)	–	91.7(4)	125(1)
$^tBu_2Cl_2Ga_2(\mu\text{-}Cl)_2$ [f]	234.2(2)	215.1(2)	197.4(5)	90.2(1)	127.2(2)

[a] Distances in pm, angles in degrees, estimated standard deviations in parentheses in units of the last digit. Cl_t = terminal Cl, Cl_b = bridging Cl.
[b] Gas phase [1].
[c] Gas phase [10].
[d] This work.
[e] Gas phase [2].
[f] Crystalline phase [11].

amplitudes and expanded to include an estimated scale uncertainty of 0.1%. Experimental and calculated intensity curves and radial distribution curves are compared in Figs. 1 and 3 respectively.

Similar refinements carried out on a *cis* model of C_{2v} symmetry led to equally good agreement between calculated and experimental intensities, $R = 0.051$ as compared to 0.049 for the *trans* model (for a definition of R see Table 1). We are thus unable to confirm the conclusions reached on the basis of ^1H NMR [6], Raman [7] and IR [7] spectra. The best values obtained for bond distances and valence angles, however, differed from those in Table 1 by less than a quarter of the quoted standard deviations.

In Table 2 we compare bond distances and valence angles in compounds of type $[X_2Y_2Ga_2(\mu\text{-}Cl)_2]$. The Ga-to-bridging-Cl bond distance is seen to decrease monotonically with increasing electron-withdrawing power of the terminal substituents, from 238 pm in $[Me_4Ga_2(\mu\text{-}Cl)_2]$, to 234 pm in $[Me_2Cl_2Ga_2(\mu\text{-}Cl)_2]$ and 230 pm in $[Cl_4Ga_2(\mu\text{-}Cl)_2]$. We suggest that the observed variation is due to an electronic effect rather than to steric factors. The bridging bond may be described as a 1:1 hybrid of normal and dative ClGa bonds, and dative bonds are known to be very sensitive to inductive effects on the acceptor atoms [12].

Acknowledgements

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