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The Molecular Structure of Bis(pentamethylcyclopentadienyl)-germanium Determined by Gas Phase Electron Diffraction

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The gas phase electron scattering pattern of bis(pentamethylcyclopentadienyl) germanium obtained with a nozzle temperature of about 140 °C, is consistent with a molecular model with D_{5h} symmetry, *i.e.* with parallel ligand rings. But models in which the angle between the ring planes is of the order of 10 or 20° cannot be ruled out. Model calculations indicate that models in which the angle is larger than 20° would lead to prohibitively short distances between methyl groups on different ligand rings. The mean Ge–C bond distance is 2.322(6) Å.

The molecular structures of dicyclopentadienyl-lead and -tin, $(\eta\text{-}C_5H_5)_2Pb$ and $(\eta\text{-}C_5H_5)_2Sn$, in the gas phase are angular:[1] In both compounds the ligand rings have at least approximate fivefold symmetry, but the rings are not parallel. In the lead compound the angle between the ring planes is 45(5)°, in the tin compound the angle is more uncertain, but has been estimated to be about 55°. In both molecules the metal atom is situated at or near the intersection of the fivefold symmetry axes of the two rings and the ten M–C bond distances are consequently approximately equal.

A recent X-ray diffraction investigation of bis(pentamethylcyclopentadienyl)tin,[2] $(\eta\text{-}C_5Me_5)_2Sn$, has shown that in this compound the angle between the ring planes is 36°, and the ten Sn–C bond distances range from 2.57 to 2.74 Å with a mean value of 2.68 Å. The apparently smaller angle between the ligand rings in $(C_5Me_5)_2Sn$ has been rationalized as being due to steric repulsions between methyl groups on different ligand rings.

$(C_5H_5)_2Ge$ has considerably lower thermal stability than the tin and lead analogues: A solid sample of the compound appears to be completely polymerized after 3 h at room temperature.[3] $(C_5Me_5)_2Ge$, recently prepared by Jutzi *et al.*[2] is, however, more stable. Since the molecular structure has been determined only for a handful of inorganic derivatives of Ge(II) and for no organic derivative, we decided to investigate the structure of $(C_5Me_5)_2Ge$ by means of gas phase electron diffraction.

EXPERIMENTAL AND STRUCTURE ANALYSIS

$(C_5Me_5)_2Ge$ was prepared as described by Jutzi *et al.*[2] The sample consisted of pale yellow crystals which melted at 90–94 °C. Thermoanalysis gave no indication of decomposition below 220 °C.

The electron scattering pattern was recorded on Balzers Eldigraph KDG-2 with reservoir and nozzle temperatures of about 140 °C. In order to keep the temperature as low as possible we used the convergent beam scattering geometry suggested by Ivanov and Zasorin.[4] We have previously used this geometry when recording the scattering pattern of bis(neopentyl)magnesium.[5]

Exposures were made with nozzle-to-plate distances of 50 and 25 cm. The optical densities of six plates from the first set and five plates from the second were processed using the programs described by Andersen *et al.*[6] The complex atomic scattering factors were calculated from an analytical representation of the atomic potential,[7] using a program written by Yates.[8] The modified experimental molecular intensity values for each nozzle-to-plate distance ranged from $s = 2.25$ to 14.00 $Å^{-1}$ with increments $\Delta s = 0.125$ $Å^{-1}$ and

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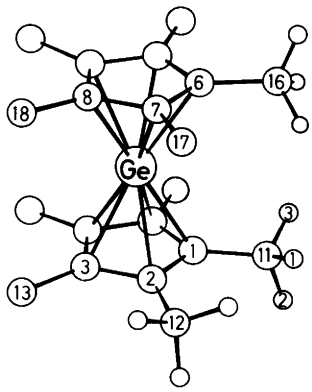

Fig. 1. Molecular model of $(C_5Me_5)_2Ge$. Symmetry D_{5h}. Most of the hydrogen atoms have been omitted for clarity.

from $s=4.50$ to 22.00 $Å^{-1}$ with increments $\Delta s = 0.250$ $Å^{-1}$.

A molecular model of $(C_5Me_5)_2Ge$ with D_{5h} symmetry is shown in Fig. 1. It was assumed that the $C-CH_3$ fragments have C_{3v} symmetry and that the methyl groups are oriented as shown in the figure. The equilibrium geometry is then determined by six independent parameters, *e.g.* the bond distances C(1)–C(2), C(1)–C(11), C–H and Ge–C, the valence angle ∠C–C–H and the angle between the C(1)–C(11) bond and the C_5 ring plane, which we denote by $\angle C_5$,C–C and define as positive when the bonds are bent *towards* the metal atom.

Table 1. Bond distances, valence angles and root mean square vibrational amplitudes of bis(pentamethylcyclopentadienyl) germanium obtained by refinement on a model of D_{5h} symmetry. (Estimated standard deviations in parentheses.)[a]

	r_a/Å	l/Å
Ge–C(1)	2.322(6)	0.136(9)
C(1)–C(2)	1.411(4)	0.043(8)
C(1)–C(11)	1.530(7)	0.053 (ass)
C(11)–H	1.120(6)	0.055(8)
Ge···C(11)	3.42	0.221(9)
Ge···H(1)	3.64	0.45 (ass)
Ge···H(2)	4.39	0.35 (ass)
C(1)···C(3)	2.28	0.047(15)
C(1)···C(12)	2.62	0.056(7)
C(1)···C(13)	3.77	0.072 (ass)
C(11)···C(12)	3.21	0.136 (ass)
C(11)···C(13)	5.19	0.097 (ass)
∠C–C–H (°)	111.4(1.0)	
∠C_5, C–C (°)	−2.7(0.9)	
h[b] (Å)	1.987(7)	

[a] For numbering of atoms see Fig. 1. [b] Perpendicular distance from Ge to the center of the C_5 ring.

Distance vectors connecting atoms in the same ligand ring were assigned the vibrational amplitudes obtained in a recent investigation of decamethylferrocene.[9] Distance vectors connecting atoms in different ligand rings were assigned amplitudes ranging from $l=0.50$ to 0.65 Å.

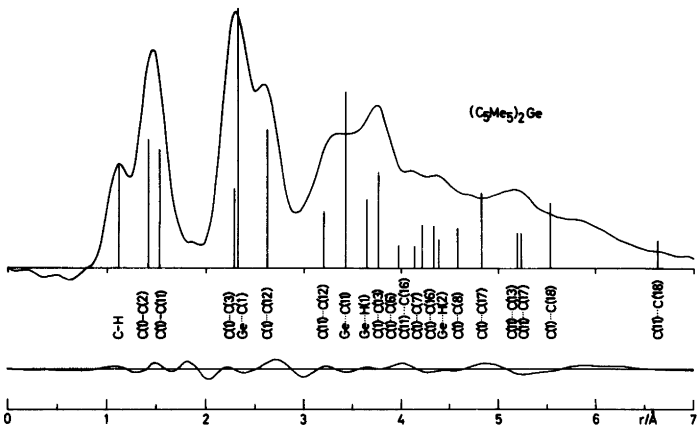

Fig. 2. Above: Experimental radial distribution curve for $(C_5Me_5)_2Ge$. Artificial damping constant $k = 0.002$ $Å^2$. Interatomic distances are indicated by bars of height proportional to the area under the corresponding peak. Below: Difference between the experimental curve and the theoretical RD curve calculated for the best model.

The six structure parameters and the six vibrational amplitudes indicated in Table 1 were refined by least-squares calculations on the intensity data, using a program written by H.M. Seip and modified by G. Gundersen.[10] The last cycles were calculated with a non-diagonal weight matrix and yielded the parameter values listed in the table.

A radial distribution curve calculated by Fourier inversion of the intensity data is shown in Fig. 2 along with the difference between this curve and a theoretical curve calculated for the best model.

Refinements were also carried out on a model of D_{5d} symmetry, *i.e.* with staggered ligand rings. For this model the interligand C···C distances proved to be less evently spaced than for the D_{5h} model (see Fig. 2), and satisfactory agreement between experimental and calculated intensities could only be obtained if these distances were assigned even higher vibrational amplitudes than for the D_{5h} model.

Since the atomic number of Ge is 32 and the molecular symmetry fairly high, we decided to test whether the neglect of three-atom scattering had any effect on our results. The calculation of this contribution was based on eqn. 14 in Ref. 11. The effect on the agreement between experimental and calculated intensities was, however, very small (R_3 [16] was reduced by 0.04 %) and the effect on the structure parameters negligible.

DISCUSSION

The mean Ge–C bond distance in $(\eta$-$C_5Me_5)_2Ge$ is 2.322(6) Å, more than 0.35 Å shorter than the mean Sn–C bond distances in $(C_5H_5)_2Sn$ [1] and $(C_5Me_5)_2Sn$ [2] and 0.45 Å shorter than the mean Pb–C bond distance in $(C_5H_5)_2Pb$.[1]

The Ge–C(1) root mean square vibrational amplitude, l=0.136(9) Å, should be regarded with some reservation: If the molecular symmetry is lower than D_{5h} (see the discussion below), the ten Ge–C bond distances are no longer required to be exactly equal, and the vibrational amplitude obtained by refinement on a symmetric model is increased to compensate for the error.

As we have seen, the diffraction data are consistent with a model with parallel rings, but this does *not* mean that angular models where the angle between the two ring planes is 10 or 20° can be ruled out: The peaks in the radial distribution function corresponding to distances between atoms in different ligand rings form an unresolved complex extending from r=4 Å and upwards. The only distinct feature of the RD-curve in this range, the peak at 5.2 Å, is due to an intra-ligand distance, C(11)···C(13). The RD-curve therefore shows that our data contain very little information about the relative position of the two rings.

In accordance with the appearance of the RD-curve, we find that satisfactory agreement is only obtained if inter-ligand distances are assigned vibrational amplitudes of the order of 0.5 Å. This might be due to non-hindered rotation of the ligand rings, to a large amplitude ring-metal-ring bending motion, or because the equilibrium structure of the molecule is, in fact, angular.

In the D_{5h} model the shortest distance between methyl groups on different rings, C(11)···C(16), is 4.1 Å, *i.e.* slightly larger than twice the accepted van der Waals' radius of a methyl group, 2.0 Å.[12] In a bent or angular model where the angle between the two planes is increased to 20°, this distance is reduced to 3.7 Å even if the rings are staggered. This is equal to the shortest distance found between methyl groups on different rings in crystalline $(C_5Me_5)_2Sn$,[2] and is certainly in the repulsive region.

The angular nature of dicyclopentadienyl-lead and -tin derivatives have been rationalized as arising from the presence of a stereochemically active lone-pair of electrons on the metal atom. In $(C_5Me_5)_2Ge$ with parallel or near-parallel rings this lone pair must be assumed to have nearly pure 4*s* character.[2]

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