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The Molecular Structure of Monomeric Methyl-
(cyclopentadienyl)zinc, $(\text{CH}_3)\text{Zn}(\eta\text{-C}_5\text{H}_5)$,
Determined by Gas Phase Electron Diffraction

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Summary

The electron scattering pattern of gaseous $(\text{CH}_3)\text{Zn}(\eta\text{-C}_5\text{H}_5)$, or $\text{MeZn}(\eta\text{-Cp})$, is consistent with a molecular model of C_{5v} symmetry (methyl H atoms excluded). The Zn-C(Me) and Zn-C(Cp) bond distances are 1.903(12) Å and 2.280(9) Å respectively. Comparison of bond distances and vibrational amplitudes indicate that the metal to ring bonding is considerably weaker in $\text{MeZn}(\eta\text{-Cp})$ than in $\text{MeBe}(\eta\text{-Cp})$.

Introduction

Wade and coworkers have prepared methyl(cyclopentadienyl)zinc, MeZnCp , and determined the crystal structure [1]. MeZnCp is monomeric in benzene, but in the crystalline phase it is polymeric. The structure may be described as consisting of puckered chains of Zn atoms each carrying a terminal methyl

group, linked by bridging Cp groups bisecting and inclined at 65° to the Zn-Zn vectors.

We have determined the molecular structure of monomeric MeZnCp by gas phase electron diffraction for comparison with the solid state structure and with monomeric MeBeCp[2].

Experimental and structure analysis

The sample of MeZnCp was a gift from Dr. K. Wade and was used without further purification. The electron scattering pattern was recorded on Balzers Eldigraph KDG-2 with a nozzle temperature of $100 \pm 10^\circ\text{C}$ and nozzle-to-plate distances of 50 and 25 cm. The optical densities of three plates from the 50 cm set and four plates from the 25 cm set were processed using the programs described by Andersen et al. [3]. The modified molecular intensity values obtained by averaging the intensity values for each nozzle-to-plate distance ranged from 2.00 to 15.00 \AA^{-1} and from 4.00 to 30.00 \AA^{-1} .

A molecular model of MeZnCp is shown in Fig. 1.

It was assumed that :

- i) The symmetry of the molecule is C_{5v} when the methyl hydrogen atoms are excluded, and ii) the ZnCH_3 fragment has C_{3v} symmetry.

No attempt was made to determine the angle of rotation of the Me group relative to the Cp ring. Refinements were carried out on the model of C_5 symmetry shown in Fig. 1.

The molecular structure is then determined by seven parameters, e.g. the bond distances $\text{C}_1\text{-H}_1$, $\text{C}_1\text{-C}_2$, Zn-C_1 , Zn-C_6 and $\text{C}_6\text{-H}_6$, the valence angle $\angle\text{Zn-C}_6\text{-H}_6$ and the angle between the C-H bonds and the C_5 plane of the Cp ring. This

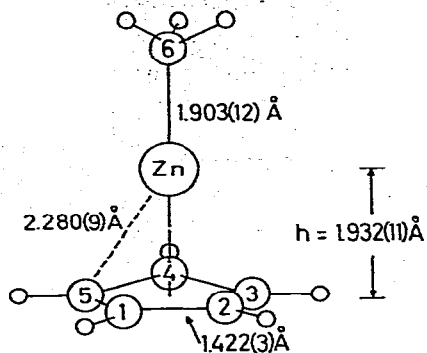


Fig. 1. Molecular model of $\text{CH}_3\text{Zn}(\text{C}_5\text{H}_5)$

angle was denoted by $\angle\text{C}_5, \text{CH}$ and defined as positive when the bonds are bent out of the plane towards the metal atom.

These parameters and seven root mean square vibrational amplitudes were refined by least-squares calculations on the intensity data from the two nozzle-to-plate distances separately, and under the constraints of a geometrically consistent r_a structure. The final refinements were carried out with a non-diagonal weight matrix using a program written by H.M. Seip [4]. The parameters obtained and their estimated standard deviations are listed in Table 1.

An experimental radial distribution curve and the difference between this curve and a theoretical curve calculated for the best model are shown in Fig. 2. The agreement is seen to be satisfactory.

Discussion

The electron scattering pattern of MeZnCp is consistent with a molecular model of C_{5v} symmetry (methyl H atoms excluded). The vibrational amplitude of the Zn-C(Cp) distances obtained by refinement of this model is however quite large,

Table 1. Bond distances (r_a), valence angles and root mean square vibrational amplitudes of $\text{CH}_3\text{Zn}(\eta\text{-C}_5\text{H}_5)$. (Estimated standard deviations in parentheses in units of the last digit).^a

	$r_a/\text{\AA}$	$u/\text{\AA}$
Zn-C(Cp)	2.280(9)	0.149(11)
Zn-C(Me)	1.903(12)	0.073(13)
C-C	1.422(3)	0.052(5)
C(Cp)-H	1.08(2)	0.077 ^b
C(Me)-H	1.12(5)	0.078 ^b
Zn...H(Cp)	2.99(4)	0.14(3)
Zn...H(Me)	2.65(4)	0.06(4)
C ₁ ...C ₃	2.301(5)	0.056 ^c
C ₁ ...C ₆	4.02(2)	0.15(2)
C ₁ ...H ₂	2.24(2)	0.101 ^c
C ₁ ...H ₃	3.35(2)	0.08(2)
h	1.932(11)	
$\angle\text{Zn-C}_6\text{-H}_6$	120(5) ^o	
$\angle\text{C}_5\text{-CH}$	1(3) ^o	

^a For numbering of the atoms consult Fig. 1. The H atoms are bonded as the C atoms to which they are bonded.

^b Assumed values.

^c Assumed equal to the corresponding amplitudes in $\text{CH}_3\text{Be}(\eta\text{-C}_5\text{H}_5)$.

$u = 0.15(1)$ Å, so less symmetrical structures, still containing a penta-hapto Cp ring, but with Zn-C(Cp) distances ranging from 2.2 to 2.4 Å, cannot be ruled out. We consider such models unlikely and base our discussion on the C_{5v} model.

MeZnCp is then isostructural with MeBeCp [2] and HBeCp [5]. However, the metal to ring bonding appears to be

considerably weaker in MeZnCp than in MeBeCp: The difference between the Zn-C(Cp) and Zn-C(Me) bond distances is 0.38 Å, while the corresponding difference in MeBeCp is 1.92 Å-1.70 Å = 0.22 Å: The Zn-C(Cp) vibrational amplitude is moreover twice as large as the Be-C(Cp) amplitude, 0.073(3) Å [2]. The loose Zn-Cp interaction may be due to poor overlap between $4p_x$ and $4p_y$ orbitals on Zn and the e_g π -orbitals of the ring and may in turn be the reason why the substance polymerises on entering the solid state.

In the solid each Zn atom is surrounded by a terminal methyl group and two bridging Cp groups, which are bonded to it in a dihapto or trihapto fashion [1]. The shortest Zn-C(Cp) distances are very similar to the Zn-C(Cp) bond distances in the monomer.

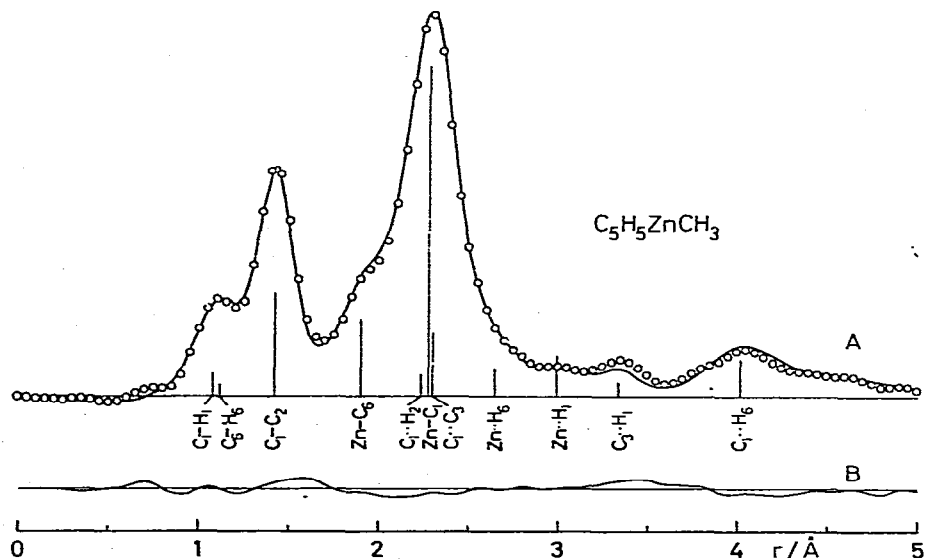


Fig. 2. A. o: experimental radial distribution curve of $CH_3Zn(C_5H_5)$. Full line: Theoretical radial distribution curve calculated for best model. Artificial damping constant $k = 0.0025 \text{ \AA}^2$. B. Difference curve.

Since they have been determined by different methods, the Zn-C(Me) bond distance in the monomer found in this study cannot be considered significantly shorter than the Zn-C(Me) bond distance found in the polymer by x-ray diffraction, 1.94 and 1.95 (1₃) Å [1], or the Zn-C bond distance in gaseous Zn(CH₃)₂ determined by rotational Raman spectroscopy, 1.929±0.004 Å [6].

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