

ELECTRON DIFFRACTION STUDY IN THE VAPOR PHASE OF THE MOLECULAR STRUCTURE OF DICYCLOPENTADIENYLZIRCONIUM DICHLORIDE

I. A. RONOVA, N. V. ALEKSEEV, N. I. GAPOTCHENKO AND YU. T. STRUCHKOV

Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R., Moscow (U.S.S.R.)

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SUMMARY

The molecular structure of $(C_5H_5)_2ZrCl_2$ has been studied by electron diffraction in the vapor phase. The molecule is a wedge-like sandwich with the inter-ring angle of 46° and bond distances of: Zr-Cl 2.309, Zr-C 2.522, C-C 1.42, C-H 1.13 Å.

After investigation of the dicyclopentadienyltitanium dichloride molecular structure¹ a question arose about factors determining a non-parallelism of the dicyclopentadienyl sandwich in this compound. Due to short metal-carbon distances there are considerable contractions of non-bonding carbon-carbon (between cyclopentadienyl rings) and carbon-chlorine distances in comparison with Van-der-Waals radii sums. Thus the Cp_2TiCl_2 molecule is severely overcrowded and one can suppose that the tilt of cyclopentadienyl rings is caused by repelling by chlorine atoms. On the other hand the cause of a sandwich wedge-like form may be attributed to the tendency of metal atom to preserve tetrahedral valence configuration which is typical for tetra-coordinated compounds of Ti^{IV} (in this case the cyclopentadienyl rings are, naturally, supposed to act as monodentate ligands). In this connection it seemed to be of interest to study the molecular structure of the analogous zirconium compound because in its molecule the metal-ring distances must be considerably longer and so steric hindrances accordingly much diminished.

Heats of formation (145 and 153 kcal/mole respectively) and ionization potentials (8.9₈ and 9.3₇ eV) of Cp_2TiCl_2 and Cp_2ZrCl_2 have similar values² and show that these molecules must be isostructural and have the same bond nature. This conclusion is supported also by their infrared and ¹H NMR spectra³⁻⁵.

Here we report the structural study of Cp_2ZrCl_2 by electron diffraction in vapour phase. The electron diffraction patterns were recorded in the EG-100 M electrograph with the r^3 sector (nozzle-to-plate distances: 400 and 200 mm). The processing of experimental data was done by our standard technique⁶. The resulting molecular intensity curve $sM(s)$ covering the interval $s=1.5-23.9 \text{ \AA}^{-1}$ is shown in Fig. 1. The structure was resolved on the basis of the radial distribution curve, the trial-and-error treatment of the $sM(s)$ curve was used also [the theoretical $sM(s)$ curves were calculated in the first Born's approximation according to the program

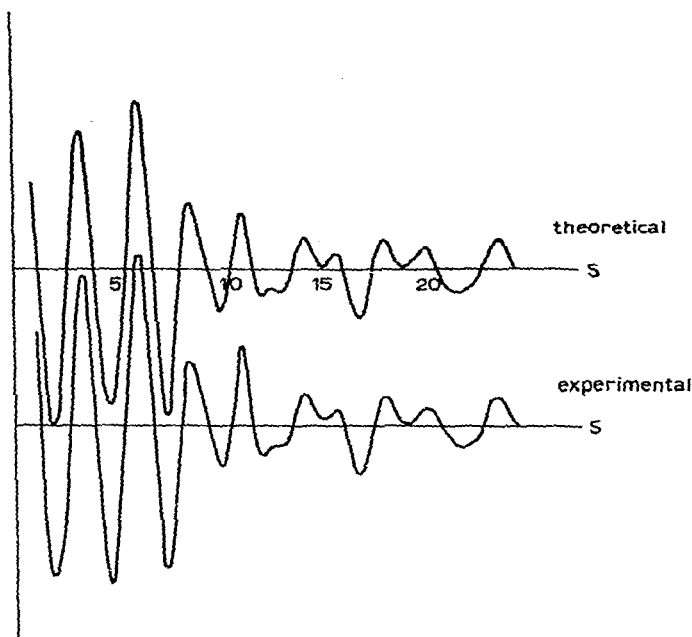


Fig. 1. The experimental intensity curve $sM(s)$ and the theoretical curve corresponding to the best molecular model.

previously described⁷]. Then non-nuclear scattering was subtracted from the experimental $sM(s)$ curve and the structure was refined by the least-squares method in a version of stage-by-stage aligning of geometrical and vibrational parameters⁸.

The internuclear distances, their root-square-mean vibrational amplitudes and bond angles are given in the Table 1.

TABLE 1

GEOMETRICAL AND VIBRATIONAL PARAMETERS OF THE Cp_2ZrCl_2 MOLECULE

Bond	r_{ij} (Å)	l_{ij} (Å)	Angle	ω_{ij} (°)
Zr-Cl	2.309 ± 0.005	0.13 ± 0.005	Cp-Zr-Cp	134 ± 5
Zr-C	2.522 ± 0.005	0.11 ± 0.005	Cl-Zr-Cl	104 ± 2
C-C	1.42 ± 0.01	0.05 ± 0.005		
C-H	1.13 ± 0.02	0.04 ± 0.01		

The dicyclopentadienylzirconium dichloride molecule is a wedge-like sandwich with non-parallel rings (Fig. 2). The Zr-C bond length (2.522 Å) is in a good agreement with previous data for monocyclopentadienyl-zirconium complexes: 2.53⁹ and 2.55¹⁰ Å in $(\pi-C_5H_5)ZrCl(CH_3COCHCOCH_3)_2$, 2.53 Å in $(\pi-C_5H_5)Zr-(CF_3COCHCOCF_3)_3$ ¹¹. The angle between ring planes equals to 46° and so is considerably smaller than the corresponding value of 59° for the Cp_2TiCl_2 molecule, although minimal non-bonding distances Cl...C are the same in both the molecules (2.95 Å). This fact shows clearly that the zirconium atom has no tendency to preserve

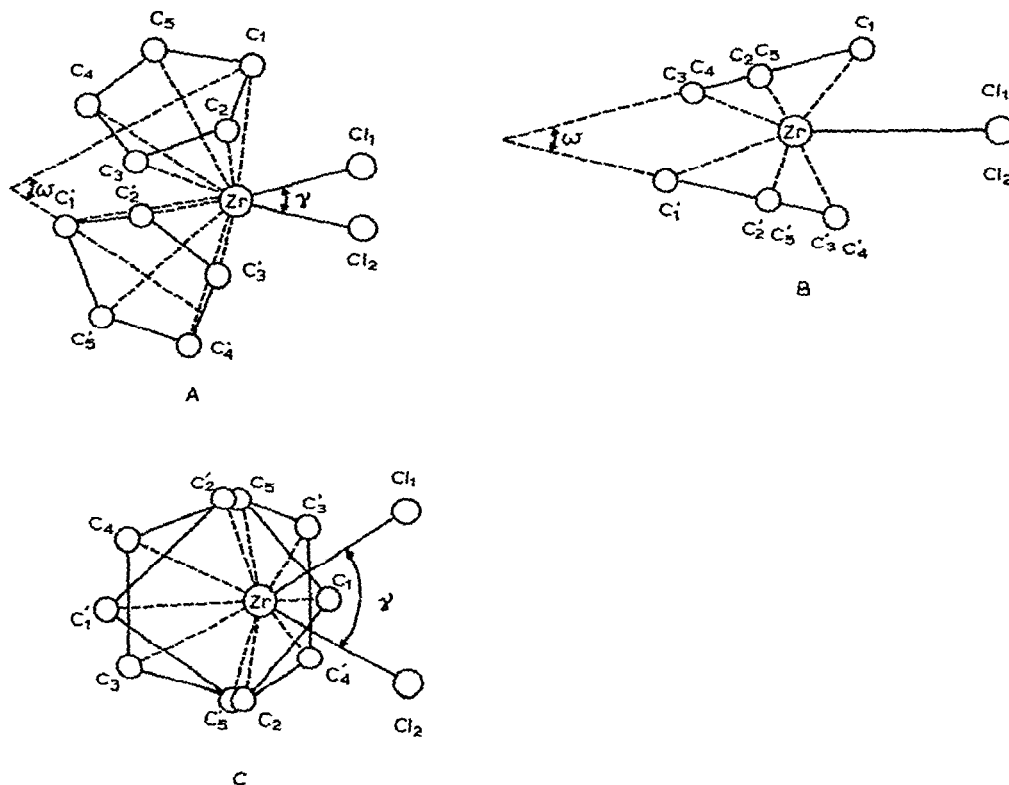


Fig. 2. Geometry of the Cp₂ZrCl₂ molecule. A: a general view; B: a projection on the plane normal to the cyclopentadienyl rings; C: a projection on the ClZrCl plane.

a tetrahedral coordination. Thus it may be concluded that the metal-ring interaction in Cp₂ZrCl₂ (and also in Cp₂TiCl₂) presents a covalent delocalized π -bond somewhat weakened due to the lack of back-donation (caused by a small number of electrons in the zirconium atom *d*-shell).

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