

X-RAY STRUCTURE OF TETRACYCLOPENTADIENYLHAFNIUM

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(Received October 21st, 1971)

SUMMARY

In the crystalline state, the molecular structure of $(C_5H_5)_4Hf$ may be described as $(h^5-C_5H_5)_2Hf(h^1-C_5H_5)_2$, and is thus similar to that of $(C_5H_5)_4Ti$ but different from that of $(C_5H_5)_4Zr$.

In previously reported studies^{1,2} of the structure of tetracyclopentadienyl-zirconium it was shown that in the crystalline state its molecular structure consists of three $h^5-C_5H_5$ rings and one $h^1-C_5H_5$ ring despite the fact that at temperatures as low as -100 to -150° the 1H NMR spectrum of this compound^{3,4} exhibits only a sharp singlet signal. $(C_5H_5)_4Hf$ has a similar 1H NMR spectrum^{4,5} but its IR spectrum differs from that of $(C_5H_5)_4Zr$ ⁶ and preliminary X-ray crystal studies^{1,2} have shown that the two compounds are not isomorphous.

In this paper the results of a more thorough X-ray study of $(C_5H_5)_4Hf$ are reported. The crystals of this material are tetragonal, $a = 9.58$, $c = 8.12$ Å, $Z = 2$, and of space group $P42_1m$. Since the compound rapidly decomposes at room temperature under X-ray irradiation, Weissenberg photographs were taken at 0° . The structure, based on 567 unique reflections, was solved by a heavy-atom technique (unfiltered Cu radiation, visual estimation of intensities) and refined by an isotropic least-squares procedure to give an R -value of 0.12.

In contrast to the structure of $(C_5H_5)_4Zr$, in the $(C_5H_5)_4Hf$ molecule two cyclopentadienyl rings are h^5 -coordinated and the other two are h^1 -bonded. The crystal structure of $(C_5H_5)_4Hf$ is partly disordered in that there are two positions of the h^1 -ring (see the thin lines in Fig. 1), which are related by a statistical mirror plane $m(x, \frac{1}{2}-x, z)$. This means that although the molecule has an intrinsic symmetry of 2, it is in the crystallographic position mm . Because of this disorder in the crystal structure it was not possible, unfortunately, to determine accurately the geometrical parameters of the h^1 -ring, although it was found that the mean C-C bond length in the h^5 -ring is 1.41 Å.

The coordination of the Hf atom in this structure is tetrahedral but severely distorted. The E-Hf-E angle (where E is the centre of the h^5 -ring) is increased to 130° and is thus closely similar to values found in other molecules with $(h^5-C_5H_5)_2M$ fragments *i.e.*, 128.7 – 136.2° in titanium compounds (see, for example, ref. 7 and papers cited therein) and 134° in $(h^5-C_5H_5)_2ZrCl_2$ ⁸. In contrast, the C-Hf-C angle is decreased to 90° , while the E-Hf-C angles have values intermediate between these two extremes.

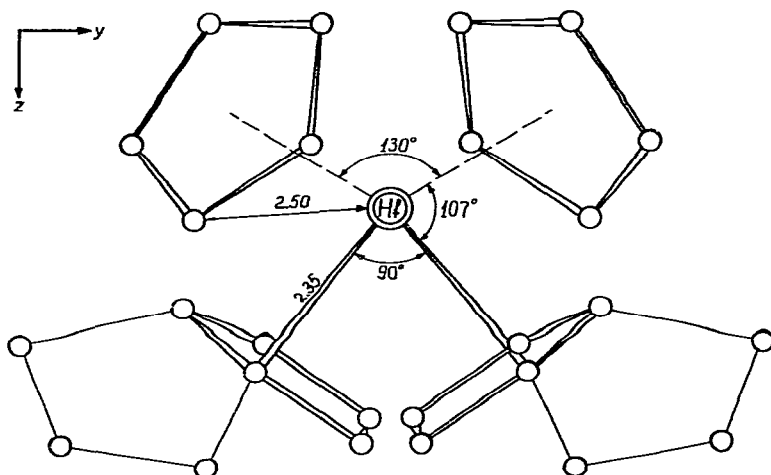


Fig. 1. Crystal structure of $(C_5H_5)_4Hf$.

The average Hf-C distance in the h^5 -rings is 2.50 Å and so is close to the value found^{1,2} in Zr complexes with one or two h^5 - C_5H_5 rings (2.52–2.55 Å). This similarity is not unexpected because the covalent radii of Zr and Hf are very nearly equal⁹. On the other hand, however, this same distance is significantly greater in $(C_5H_5)_4Zr^{1,2}$ (2.64 Å). The Hf-C (h^1 - C_5H_5) bond in $(C_5H_5)_4Hf$ is also shorter (2.35 Å) than the Zr-C σ -bond in $(C_5H_5)_4Zr$ (2.47 Å), although in this case little significance can be placed on this difference since it is virtually equal to the experimental error imposed on the results through the h^1 - C_5H_5 ring disorder present in the structure of $(C_5H_5)_4Hf$. A similar increase in the U-C (and U-Cl) bond length has been found¹⁰ in $(C_5H_5)_3UCl$, in which three h^5 - C_5H_5 rings, *i.e.* more than two, exist.

Thus, the structure of the $(C_5H_5)_4Hf$ molecule in the crystalline state appears to be similar to that of $(C_5H_5)_4Ti^4$ although an intermediate member of the series, $(C_5H_5)_4Zr$, has a different molecular structure. This result illustrates yet again the flexibility of the cyclopentadienyl ring in its bonding with different metals, a flexibility which is demonstrated by the rapid exchange of h^1 - and h^5 -rings when these compounds are present in solution¹¹.

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