The Crystal Structure of Zirconium(IV) Borohydride (at −160°)

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SEVERAL simple transition-metal borohydrides have been characterized, but no unequivocal determination of their stereochemistry has been reported.[1] The stoicheiometry of zirconium borohydride has been established[2] as $Zr(BH_4)_4$, but the number of bridging hydrogen atoms from each borohydride ligand has not been directly ascertained, although it is customarily assumed that *two* hydrogen bridges link the boron to the central metal atom. [^1H and ^{11}B n.m.r. studies are not helpful in resolving this problem, because of exchange processes.[1]] The infrared spectrum of $Zr(BH_4)_4$ has been reported, and has been interpreted[1] in terms of molecular D_{4d} (or D_{4h}) symmetry (*i.e.*, a square-planar arrangement of boron atoms about the zirconium).

In order to obtain direct information on the stereochemistry of $Zr(BH_4)_4$, a complete three-dimensional single-crystal *X*-ray structural analysis of the compound has been undertaken. The structure was solved by conventional Fourier and least-squares refinement techniques, the present discrepancy index being $R = 6{\cdot}55\%$ for 100 independent reflections (~90% of the observable sphere) collected on film from a crystal maintained at −160° c. The compound crystallizes in the cubic space group $P\bar{4}3m$ (no. 215) with $a = 5{\cdot}86$ Å and $Z = 1$. Thus, provided there is no disorder, the molecule must possess the full T_d ($\bar{4}3m$) symmetry of the space group. The refined structural analysis confirms the T_d symmetry of the molecule. The zirconium atom is tetrahedrally surrounded by four crystallographically equivalent boron atoms ($Zr \cdots B = 2{\cdot}34 \pm 0{\cdot}03$ Å), the symmetry of the space group requiring that each $Zr \cdots B$ vector is coincident with a C_3 axis. A *single* terminal hydrogen atom has been located on this threefold axis ($Zr \cdots B\text{–}H = 180°$, $B\text{–}H = 1{\cdot}2 \pm 0{\cdot}4$ Å*).

Although diffraction ripples in the vicinity of the zirconium atom preclude the reliable location of bridging hydrogen atoms on the electron density map, it is apparent that there are *three* such atoms associated with each borohydride ligand. Thus (at −160°) the zirconium atom is surrounded by twelve bridging hydrogen atoms, as is shown in the Figure.

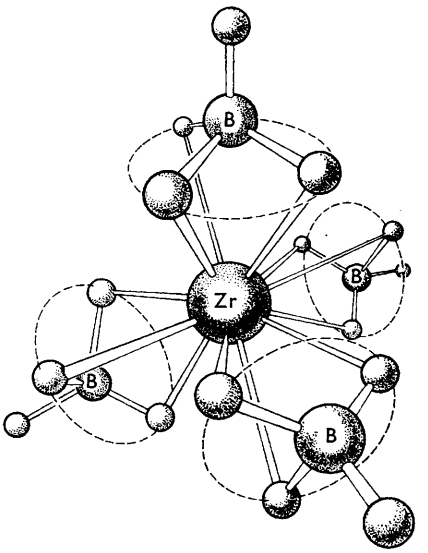

FIGURE. *One of the possible ordered arrangements of borohydride groups about the zirconium atom.* [*The other possibility involves the rotation of each set of bridging hydrogen atoms by* 60°.]

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* Although there is a large estimated standard deviation on this parameter, the location of this terminal hydrogen atom is definite. It has appeared on each observed and difference Fourier throughout the analysis.

[1] B. D. James, R. K. Nanda, and M. G. H. Wallbridge, *J. Chem. Soc.* (*A*), 1966, 182, and references therein.
[2] H. R. Hoekstra and J. J. Katz, *J. Amer. Chem. Soc.*, 1949, **71**, 2488.