Gas-phase Nuclear Magnetic Resonance Spectroscopic Study of the Molecular Structure of Beryllium Borohydride, Be(BH₄)₂

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Summary
Gas-phase and solution n.m.r. spectral studies of beryllium borohydride, Be(BH₄)₂, indicate that it contains magnetically equivalent BH₄ groups that undergo rapid internal hydrogen exchange; previously postulated triangular boron-beryllium-boron molecular configurations are inconsistent with the n.m.r. data.

The gas-phase structure of beryllium borohydride, Be(BH₄)₂, has been a subject of some controversy. As many as nine different structures have been proposed for the gas-phase monomer with varying degrees of supporting evidence based primarily on vibrational, electron diffraction, and dipole moment studies. Several theoretical studies have also been undertaken. The solid-state structure of Be(BH₄)₂ has been shown to be a helical polymer by a single-crystal X-ray diffraction study.

In spite of these efforts, unambiguous experimental evidence defining the gas-phase structure of Be(BH₄)₂ has not been reported. We report here the results of ambient gas-phase and solution ¹¹B and ¹H n.m.r. spectral studies of Be(BH₄)₂.

Beryllium borohydride was prepared by the method of Schlesinger, Brown, and Hyde and was handled using standard high-vacuum techniques. ¹¹B and ¹H n.m.r. spectra (86.7 and 270 MHz, respectively) of Be(BH₄)₂ were obtained on a Bruker WH-270 F.T.n.m.r. spectrometer. The gas-phase spectra, the boron probe was modified to eliminate borosilicate glass, and the samples were contained in 5 mm quartz tubes in order to eliminate background boron signals. ¹H spectra were also obtained on a Varian XL-100 F.T.n.m.r. spectrometer using a 12 mm o.d. Pyrex sample tube. The ¹H spectra showed significant probe backgrounds unique to each instrument. Spectra were obtained at ambient temperature (ca. 23 °C) on saturated-vapour samples containing partial pressures of ca. 6 Torr of Be(BH₄)₂ and 2—5 atm of inert gas (CD₃)₂Si and/or argon to effect collision narrowing of the spectral lines. Solution-phase spectra were obtained using [²H₆]benzene and [²H₆]dichloromethane solvents.

The gas-phase ¹¹B and ¹H n.m.r. spectra of Be(BH₄)₂ shown in Figure 1, indicate the presence of a single species. The ¹¹B spectrum consists of a 1:4:6:4:1 quintet that arises from equivalent boron atoms, each of which is coupled to four equivalent hydrogen nuclei $J(¹¹B-H) = 87$ Hz. The ¹H spectrum is a 1:1:1:1 quartet indicating that all hydrogen atoms are equivalent and are coupled to a single ¹¹B (80%, $I = 3/2$) nucleus [small resonances due to coupling to ⁴²Be (20%, $I = 3$) are also present]. The ¹¹B spectrum shows the presence of a small amount of diborane(6) [$S(½)$ p.p.m. downfield from the Be(BH₄)₂ signal], a decomposition product which accumulates during the course of the spectral acquisition (ca. 12 h). No line-shape features of the ¹¹B or ¹H spectra require the invocation of ⁴²Be (I = 3/2) coupling, nor have such couplings been identified in the spectra of alkyl beryllium hydrides.

The solution spectra exhibit the same patterns and the same coupling constants as are observed for the gas-phase spectra ($¹¹B: δ = 36.2$ ppm; BF₃OEt₂ = 0, $J = 86$ Hz, in [²H₆]benzene; $¹¹B: δ = 0.4$ ppm; Me₃Si = 0, $J = 86$ Hz in [²H₆]benzene).

Figure 1. Gas-phase n.m.r. spectra of Be(BH₄)₂. (a) ¹¹B spectrum at 86.6 MHz. (b) ¹H spectrum at 100 MHz.

Figure 2

The n.m.r. spectra can be interpreted only in terms of a Be(BH₄)₂ structure containing magnetically equivalent borohydride groups. Within each borohydride group rapid internal hydrogen exchange takes place on the n.m.r. time scale. None of the previously postulated (see refs. 2, 3, and 6) or remotely possible triangular Be(BH₄)₂ structures are consistent with these spectra, regardless of the mechanism of hydrogen exchange. However, an exchange mechanism...
involving rapid transformation from one linear B-Be-B configuration to another, such as that depicted in Figure 2, is consistent with the observed n.m.r. spectral data.

All uncontroversial Be-BH₄ interactions [solid, polymeric Be(BH₄)ₓ,¹⁷ (MeBeBH₄)ₓ,²⁰,²¹ and solid B₂H₆BeBH₄,²²] indicate the presence of double hydrogen bridges between beryllium and the borohydride boron. Theoretical studies have favoured either double or triple hydrogen bridges and a linear B-Be-B framework.¹⁴⁻¹⁶ Most recent i.r. spectral studies suggest either double or triple hydrogen bridges.¹³⁻¹⁵ Thus, gas-phase monomeric Be(BH₄) is highly fluxional on the n.m.r. time scale and, based on the present as well as previous studies,¹⁻¹² undoubtedly has a linear B-Be-B framework in which local configurational interchange results in rapid hydrogen exchange within each borohydride group.

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