the formation of crystalline BN.

Although, in its present form, the chemistry outlined here does not result in a fusible or soluble preceramic polymer, the results indicate that partially ordered hexagonal boron nitride powder can be readily obtained from the pyrolysis of a solid, insoluble poly(borazinylamine) precursor, **2**, that is easily formed from the well-known borazene monomer $[(Me_2N)BNH]_3$ and NH_3. The precise identity of the insoluble poly(borazinylamine) polymer was not elucidated in detail; however, observations made in TGA and bulk pyrolysis studies are consistent with the occurrence of a series of complex aminoborazine deamination cross-linking reactions, followed by borazene ring-opening, elimination–condensation processes of a type described earlier.[5,10] These observations suggest additional approaches for manipulating aminoborazene monomers, and extensions are being evaluated.

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Supplementary Material Available: Figures showing a typical TGA plot and a powder X-ray diffraction pattern (2 pages). Ordering information is given on any current masthead page.

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(19) The TEM micrographs are similar to those reported previously in our work,[8] except that the particles are larger and the lattice fringes are more well-defined.

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Inelastic Neutron-Scattering Study of $K[HCo_6(CO)_{15}]$: Implications for Location of the Hydride

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The study of transition-metal hydride complexes by vibrational spectroscopy has been of considerable utility in elucidating details of hydrogen–metal interactions.[2,3] Inelastic neutron-scattering (INS) techniques have in this context often proved invaluable[4] in assigning modes involving the hydrogen atoms because of the high sensitivity of INS to hydrogen. While many such systems where hydrogen atoms bridge two or more metal atoms have served as models for hydrogen chemisorbed on surfaces,[2,4] a much more limited number of metal complexes[5-8] are known to contain interstitial hydrogen. These in turn may be good representations of interstitial hydrogen either inside or just below the surface of bulk metals. An example of the latter, subsurface hydrogen, has been observed in Pd.[9] In fact, some of these compounds involve metal atoms (Co,[5] Ru[6]) that do not readily form hydride phases in the bulk and therefore are of particular importance in the study of metal hydrides.

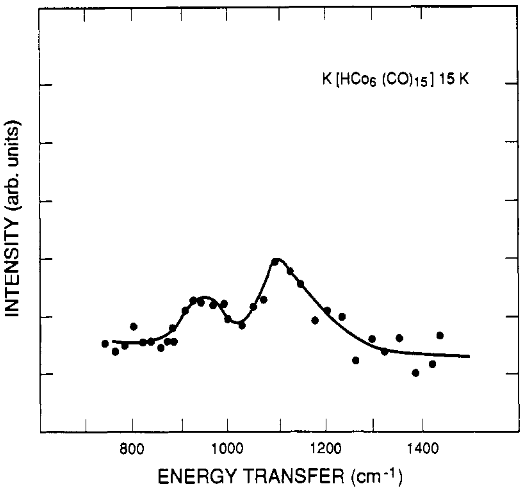

Figure 1. Neutron vibrational spectrum of the hydride in $K[HCo_6(CO)_{15}]$ obtained by subtraction of the spectrum of the deuterated form from that of the hydrogenated form. The line is drawn as a guide for the eye.

One such system is the ion $[HCo_6(CO_{15})]^-$, which is known from a single-crystal neutron diffraction study[5] to have a hydrogen atom located very nearly in the center of the Co_6 octahedron. One would therefore expect to observe a triply degenerate ν(M–H) mode, since the observed variation of metal–hydrogen distances is relatively small (i.e. 1.80 (2)–1.87 (2)Å). An INS study by Graham et al.[10] was indeed successful in assigning a single, relatively sharp band at 1056 cm^{-1} as ν(M–H). The compound used in the latter study used Cs^+ as the counterion, while the single crystal in the diffraction work contained $[(Ph_3P)_2N]^+$ instead.

Recently, Stanghellini and Longoni obtained IR vibrational spectra of several interstitial hydride clusters[11] including $K[HCo_6(CO)_{15}]$. They, however, assigned two bands, at 1086 and 949 cm^{-1}, respectively, to two ν(Co–H) modes. The experiments were performed at room temperature and at 100 K with the samples in Nujol mulls and, also, in alkali-metal halide disks. In the latter case, the spectra were found to change: repeated grinding and pressing of the sample in the alkali-metal halide disks caused the band at 949 cm^{-1} to virtually disappear whereas a rather weak line at ca. 1060 cm^{-1} increased considerably in intensity.[11] Changes were also observed in the CO deformation region with treatment of the alkali-metal halide disk samples.

The assignment of the two lines to ν(Co–H) was, however, unambiguous on account of the clearly observed isotope shift. We have, therefore, undertaken INS studies on the same compound $K[HCo_6(CO)_{15}]$ in an attempt to resolve the apparent discrepancy with the prior INS study by Graham et al.[10] The compound was prepared by the method described in ref 5. INS spectra were obtained for both the hydrogenated and deuterated compounds on the filter difference spectrometer (FDS)[12] at the Los Alamos Neutron Scattering Center. Since the neutron-scattering cross section for D is more than 1 order of magnitude less than that

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of H, the modes involving the former are essentially not visible in the present case, where only 1 in 38 atoms is D and only small samples (~2 g) were available. This sample therefore served as a "blank", and its INS spectrum was subtracted from that of the hydrogenated compound to thereby isolate[13] those vibrations involving mainly the hydrogen atom. The resulting difference spectrum (Figure 1) obtained by using the Be analyzers of the FDS only shows two broad peaks, at approximately 940 and 1100 cm^{-1} in the region of interest. These data are therefore in qualitative agreement with the IR results on Nujol mulls and on CsI disks before additional grinding and pressing was done on the latter. Small differences in the peak positions in the INS data compared with optical data are not uncommon and are often the result of the relatively large value of momentum transfer used in the neutron studies.

It appears therefore that the hydrogen vibrational spectrum is dependent on the nature of the counterion, since the INS data for the Cs^+-containing compound shows just one line, whereas, in the K^+ analogue, two well-separated INS bands are observed. The former is thus consistent with the approximately centered position of H determined by the crystal structure study (with $[(Ph_3P)_2N]^+$ counterion), while the present data suggest that at least some hydrogen atoms are located in less symmetric sites.

We may attempt a consistent assignment of the principal features of the spectra in the present work, the prior INS study,[10] and the IR absorption work[11] by assuming that the band(s) in the region 1050–1100 cm^{-1} are assigned to ν(Co–H) for μ_6-H. The reason for this assumption is that all experimental data to date have these bands in common. The additional peak observed by INS and IR[11] spectroscopy at ca. 950 cm^{-1} would then have to be associated with a different hydride, most likely doubly or triply bridging two or three Co atoms. In either case, the 950-cm^{-1} line should be accompanied by another excitation in the frequency range of these experiments. For μ_3-H a doubly degenerate ν_{as}(Co–H) should be observed in addition to ν_s(Co–H). Vibrational data on such systems[3] suggest that the two lines should have frequencies within ±20% of each other. There is, however, no strong line within this range about 950 cm^{-1} that could unambiguously be so assigned, but a weak peak at about 1150 cm^{-1} in the IR[11] data does show the expected isotropic shift, and the present INS spectrum appears to have a shoulder in this frequency range. Since the INS intensity of the doubly degenerate ν_{as} would be about twice that of the nondegenerate ν_s, the former would be assigned at 950 cm^{-1} and the latter at 1150 cm^{-1}.

Extensive compilations of data[2] on μ_2-H show that, for a deformation mode ν_2 at 950 cm^{-1}, the antisymmetric stretch ν_3 would be expected to occur at about 1800 cm^{-1}. Since this frequency is well outside the range of the experimental studies in question, a doubly bridging hydride remains a possibility as the second hydrogen species in the K^+ compound.

From the intensities of the INS bands, one may then conclude that somewhat more than half of the hydrogen in $K[HCo_6(CO)_{15}]$ is located in the interstitial site with the rest most likely in either μ_2-H or μ_3-H form on the inside (or possibly outside) of the Co cluster. In the Cs^+ analogue, however, as well as the $[(Ph_3P)_2N]^+$ system studied by neutron diffraction, essentially all the hydrogen is found to be in the interstitial site. One is thus led to the conclusion that the μ_6-H coordination in these complexes is highly sensitive to the surroundings of the complex such as the type of counterion used in the preparation of the solid.

The essential result of the present INS study then is that there is substantial agreement with those vibrational features that were unambiguously assigned to ν(Co–H) in the IR work[11] on $K[HCo_6(CO)_{15}]$ and that vibrational band(s) in the region 1050–1100 cm^{-1} are most likely to be associated with μ_6-H in these octahedral Co clusters.

Further work will be aimed at identifying the hydride species that gives rise to the excitation at ca. 950 cm^{-1}, which, in fact, is found[11] to disappear upon repeated grinding and pressing of $K[HCo_6(CO)_{15}]$ in alkali-metal halide disks. Diffraction studies of the K^+ or Cs^+ salt (instead of $[(Ph_3P)_2N]^+$) will be undertaken to locate the noninterstitial hydrogen. It may also be worthwhile to perform an INS study of the Ru analogue, $[HRu_6(CO)_{18}]^-$, where a two-peak spectrum associated with H was observed,[14] while neutron diffraction work[6] showed the hydride to be located on the interestitial site. The suggestion that one of these arises from a Fermi resonance could thereby be tested.

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Additions and Corrections

1988, Volume 27

Boon K. Teo* and Hong Zhang: Magic Numbers in Atom and Electron Counting of Supraclusters Based on Vertex-Sharing Icosahedra.

Page 416. The G_7, S_7, B_7, T_7, and N_7 values of $s_7(75)$, the pentagonal-bipyramidal array of seven vertex-sharing icosahedra (cf. Figure 1f), should be 75, 67, 43 or 46, 445 or 448, and 890 or 896, respectively.—Boon K. Teo