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PREPARATION AND PROPERTIES OF THE ACTINIDE BOROHYDRIDES: $Pa(BH_4)_4$, $Np(BH_4)_4$, and $Pu(BH_4)_4$†

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ABSTRACT

The actinide borohydrides, $Pa(BH_4)_4$, $Np(BH_4)_4$, and $Pu(BH_4)_4$ have been synthesized. $Pa(BH_4)_4$, a solid at 20° is isostructural with $U(BH_4)_4$. $Np(BH_4)_4$ and $Pu(BH_4)_4$ are volatile liquids at 20° but are isostructural at low temperatures and crystallize in a tetragonal crystal structure type. The metal atom distances indicate the solid is monomeric and similar to $Zr(BH_4)_4$. Preliminary Raman spectra on solid $Np(BH_4)_4$ support this idea. Gas-phase infrared spectra indicate the Np and Pu atoms in these compounds are surrounded by four BH_4^- groups in a tetrahedral array with each B coordinated via 3 hyrodgen bridge bonds to the metal atom.

Sir:

Uranium(IV) borohydride, a volatile dark green solid, was first synthesized during the Manhattan Project.[1] Hoekstra and Katz[2] reported the preparation of the much less volatile, but isostructural, $Th(BH_4)_4$ in 1949. Recently uranium borohydride[3,4] and its etherate complexes[5] have again been the subject of structural and spectroscopic investigations. As part of our program on the properties of actinide borohydrides, we report in this communication the syntheses of $Pa(BH_4)_4$, $Np(BH_4)_4$, and $Pu(BH_4)_4$, the remaining borohydride complexes of the first five elements of the actinide series, and some of their physical properties.[6]

All five actinide compounds, $An(BH_4)_4$, are made by the solvent-free reaction of the anhydrous tetrafluoride with $Al(BH_4)_3$, viz.

$$AnF_4 + 2Al(BH_4)_3 \rightarrow An(BH_4)_4 + 2AlF_2BH_4 \quad .$$

One of the important properties characteristic of the metal borohydrides is their high volatilities, enabling them to be pumped out of the reaction mixture and purified by trap-to-trap sublimation. The vapor pressures increase with higher atomic number of the metal. $Th(BH_4)_4$, which sublimes at 120° in vacuum, exerts a pressure of .2mm Hg at 150°[2] while Np and Pu borohydrides easily sublime at -10°. $Np(BH_4)_4$ has a vapor pressure of 10mm Hg at 25° making it the most volatile compound of tetravalent Np known to date. $Pu(BH_4)_4$ appears to exhibit a vapor pressure similar to $Np(BH_4)_4$.

The synthesis of $Pa(BH_4)_4$ follows that of $Th(BH_4)_4$ by Hoekstra and Katz[2], but the reaction tube was modified by the addition of a demountable cold finger from which the $Pa(BH_4)_4$ could be removed in an inert atmosphere dry box. $Pa(BH_4)_4$ is an orange, air sensitive solid sublimable at 55° in vacuum. X-ray powder diffraction photographs have shown that it is isomorphous with the uranium and thorium borohydrides. Its tetragonal unit cell with $a = 7.54(3)$Å and $c = 13.23(5)$Å contains four molecules, giving a calculated density of 2.63 g/cm^3.

The method used for making Np and Pu borohydrides differs from that above because their high volatilities require no cold finger and their thermal instabilities demand that the reaction be carried out at a lower temperature and for a shorter time. We have found that carrying out the reaction at 0° for 4 hours works well after which time the $An(BH_4)_4$ and unreacted $Al(BH_4)_3$ are collected in -78° and -196° traps, respectively. Yields were increased by returning the unused $Al(BH_4)_3$ to the reaction tube for another 4 hour period and repeating this procedure several times until no more $An(BH_4)_4$ was obtained. An earlier attempt to make $Np(BH_4)_4$ was reported[7] in which only a green, nonvolatile solid was obtained in the reaction vessel. This was probably a mixture of NpF_4 and mixed Np fluoroborohydrides due to the presence of either metallic impurities (e.g., NiF_2) and/or improper reaction conditions. Hoekstra and Katz[7] noted a color change in their PuF_4/$Al(BH_4)_3$ reaction vessel from tan to blue-green, the same color change we observe in ours, however, their $Pu(BH_4)_4$, if it did form, must have decomposed before collection, as they obtained no volatile Pu compound.

$Np(BH_4)_4$ is a dark green, pyrophoric liquid which melts at 14.2°. It must be kept in a greaseless storage tube under liquid nitrogen since it decomposes fairly rapidly at 25° transforming into a yellow, nonvolatile solid with the evolution of H_2 and B_2H_6. This observation suggests that $Np(BH_4)_3$ is formed. At higher temperatures a shiny, metallic mirror is obtained which may be Np metal or NpB_4. $Pu(BH_4)_4$ is a bluish-black liquid with properties very similar to $Np(BH_4)_4$ but is even more unstable to thermal decomposition.

Diffraction patterns recorded with a low-temperature x-ray powder camera show that $Pu(BH_4)_4$ and $Np(BH_4)_4$ are isomorphous and have a new tetragonal crystal structure type, with a = 8.59(1)Å, c = 6.1(2)Å at -20°C for the Pu compound and a = 8.54(5)Å, c = 6.1(2)Å at -150°C for the Np compound. The low accuracy of the c dimensions is the result of strong preferred orientation of the crystals and absence from the films of reflections with ℓ values greater than 2. The unit cell contains two metal atoms at 0,0,0 and 1/2,1/2,1/2. No reflections were observed which indicate any deviation from body-centered symmetry. The diffraction data do not define the boron and hydrogen positions.

Each metal atom has two metal atom neighbors at 6.1Å and eight more at 6.8Å. These distances indicate that the solid is monomeric, like $Zr(BH_4)_4$[8] and $Hf(BH_4)_4$,[3b] rather than polymeric with borohydride bridges like those in $U(BH_4)_4$.[3a] The molecular volumes (225, 222, 186, 201, and 211Å^3, respectively, for the Pu, Np, U, Zr, and Hf compounds) suggest the same conclusion. The metal atom positions in $Pu(BH_4)_4$ are closely related to those in solid $U(BH_4)_4$, but are more symmetrical.

The structure can be converted into the $Zr(BH_4)_4$-type structure with little distortion if molecules at 1/2,1/2,1/2 are moved to 1/2, 1/2,0.

The room temperature gas phase IR spectra of Hf, Np, and Pu borohydrides and of U borohydride at 50°(Fig. 1) were taken on a Perkin-Elmer 283 IR spectrophotometer with the sample contained in a 10cm cell fitted with KBr windows. It can be seen that the Np and Pu compounds have similar spectra to $Hf(BH_4)_4$ in which four BH_4^- groups surround the metal in a tetrahedral array each coordinated via 3 hydrogen bridge bonds making the metal 12-coordinate.[9]

Our preliminary Raman spectrum on solid $Np(BH_4)_4$ at -85° is equivalent to that for single crystal $Hf(BH_4)_4$ [9a] if one allows for effects due to the heavier Np atom. This reinforces our belief that $Np(BH_4)_4$ is a monomer in the solid state. Since polymeric linkages need not be broken upon vaporizing, $Np(BH_4)_4$ and $Hf(BH_4)_4$ therefore have much higher vapor pressures than $U(BH_4)_4$ which was shown to be a monomer and of the same structure as $Hf(BH_4)_4$ in the gaseous state.[9b,10]

Further studies are underway on the spectroscopic, structural, and magnetic properties of these new actinide borohydrides.

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FIGURE CAPTION

Figure 1. Gas phase infrared spectra of metal borohydrides. The spectrum of $U(BH_4)_4$ was run at 50° in order to have sufficient vapor pressure. Peaks at 2522, 2345, 1604, and 1175 cm^{-1} were due to B_2H_6, a decomposition product.

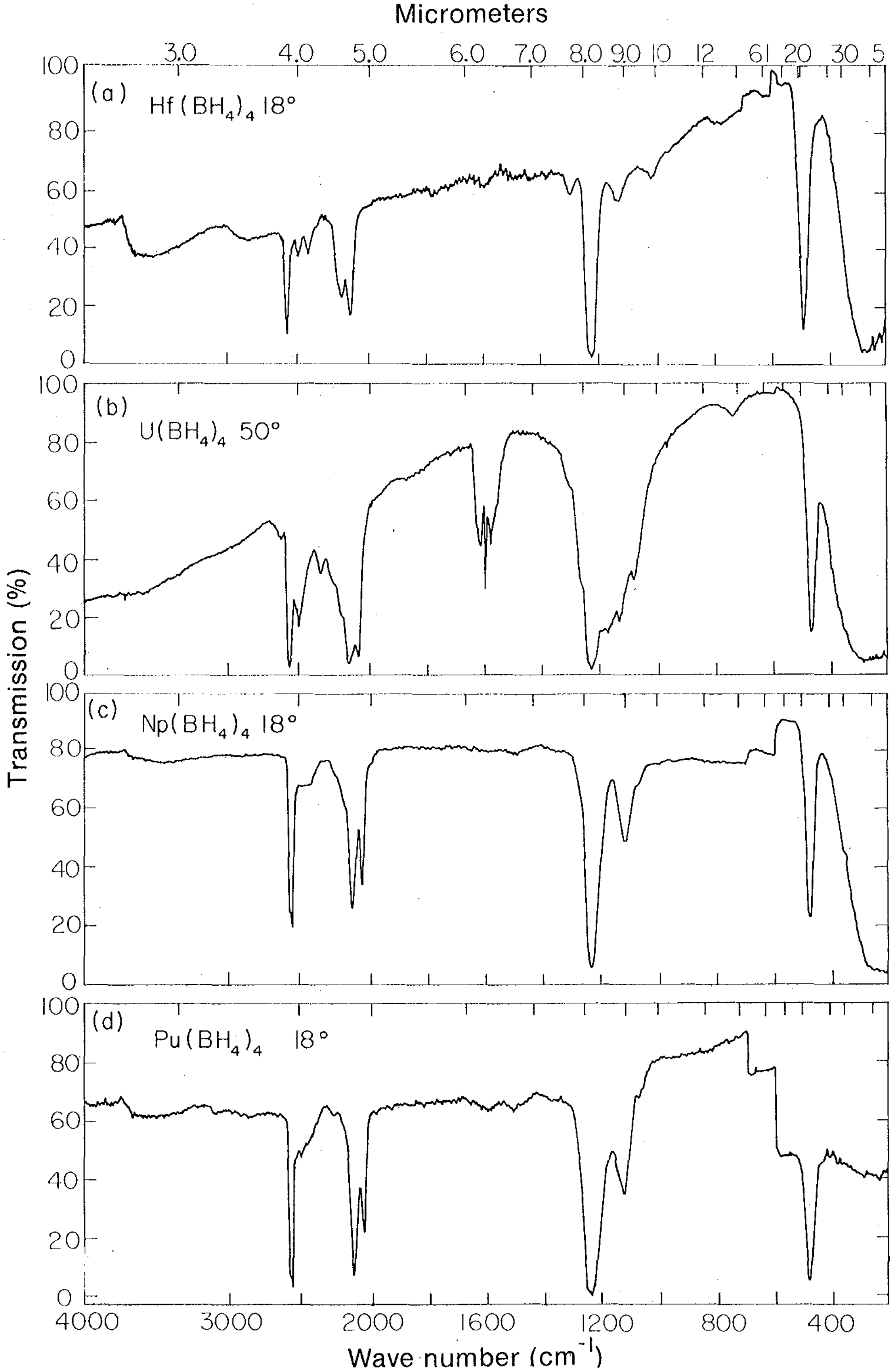
Micrometers
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
16
20
30
50
(a) Hf(BH$_4$)$_4$ 18°
(b) U(BH$_4$)$_4$ 50°
(c) Np(BH$_4$)$_4$ 18°
(d) Pu(BH$_4$)$_4$ 18°
Transmission (%)
0
20
40
60
80
100
4000
3000
2000
1600
1200
800
400
Wave number (cm^{-1})
XBL772-397

Fig. 1