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Preparation and Properties of the Actinide Borohydrides: Pa(BH4)4, Np(BH4)4, and Pu(BH4)4[1]

Sir:

Uranium(IV) borohydride, a volatile dark green solid, was first synthesized during the Manhattan Project.[2a] Hoekstra and Katz[2b] 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 synthesis of $Pa(BH_4)_4$, and the first successful syntheses of $Np(BH_4)_4$ 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.

$$AnF_4 + 2Al(BH_4)_3 \rightarrow An(BH_4)_4 + 2AlF_2BH_4$$
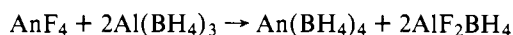
One of the important properties characteristic of the metal borohydrides is their high volatilities, enabling them to be pumped out of the reaction mixture and purified by trap-to-trap sublimation. The vapor pressures increase with higher atomic number of the metal. $Th(BH_4)_4$, which sublimes at 120 °C under vacuum, exerts a pressure of 0.2 mmHg at 150 °C,[2b] while neptunium and plutonium borohydrides easily sublime at −10 °C. $Np(BH_4)_4$ has a vapor pressure of 10 mmHg at 25 °C making it the most volatile compound of tetravalent Np known to date. $Pu(BH_4)_4$ appears to exhibit a vapor pressure similar to that of $Np(BH_4)_4$.

The synthesis of $Pa(BH_4)_4$ follows that of $Th(BH_4)_4$ by Hoekstra and Katz,[2b] 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 drybox. $Pa(BH_4)_4$ is an orange, air-sensitive solid sublimable at 55 °C under 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) and $c = 13.23$ (5) Å contains four molecules, giving a calculated density of 2.63 g/cm³.

The method used for making neptunium and plutonium 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 °C for 4 h works well, after which time the $An(BH_4)_4$ and unreacted $Al(BH_4)_3$ are collected in −78 and −196 °C traps, respectively. Yields were increased by returning the unused $Al(BH_4)_3$ to the reaction tube for another 4-h 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. The solid was probably a mixture of NpF_4, mixed neptunium fluoroborohydrides, or lower neptunium borohydrides due to 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 that 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 °C. It must be kept in a greaseless storage tube under liquid nitrogen since it decomposes in the liquid phase fairly rapidly at 25 °C 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 decomposes more rapidly in the liquid phase.

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) and $c = 6.1$ (2) Å at −20 °C for the Pu compound and $a = 8.54$ (5) and $c = 6.1$ (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 >2. The unit cell contains two metal atoms at 0,0,0 and ½,½,½. 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 6.1 Å and eight more at 6.8 Å. 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 211 Å³, respectively, for the Pu, Np, U, Zr, and Hf compounds) suggest

Table I. Physical Properties of the Actinide Borohydrides and Hafnium Borohydride

Compd	Color	Stability (20 °C)	Mp, (°C)	Vapor pressure (mmHg)/°C	M^{4+} radius, Å	Solid	Gas phase molecular symmetry	Density, g/cm⁻³
$Th(BH_4)_4$[a]	White	Stable	203 dec	0.05/130	0.972[d]	Polymeric	T_d?	2.56
$Pa(BH_4)_4$	Reddish Orange	Stable	Dec		0.935[d]	Polymeric	T_d?	2.63
$U(BH_4)_4$[b,c]	Dark Green	Very slow dec	Dec	0.3/34	0.918[d]	Polymeric	T_d	2.71
$Np(BH_4)_4$	Bluish Green	Dec	14	10/25	0.903[d]	Monomeric	T_d	2.21
$Pu(BH_4)_4$	Bluish Black	Dec	~14	~10/25	0.887[d]	Monomeric	T_d	2.20
$Hf(BH_4)_4$[a,e]	White	Very slow dec	29	15/25	0.79	Monomeric	T_d	1.86

[a] Reference 2a. [b] Reference 2b. [c] Reference 3a. [d] G. T. Seaborg, "Encyclopedia of Chemical Technology", Vol. 1, 3rd ed, Wiley, New York, N.Y., 1978. [e] Reference 9a.
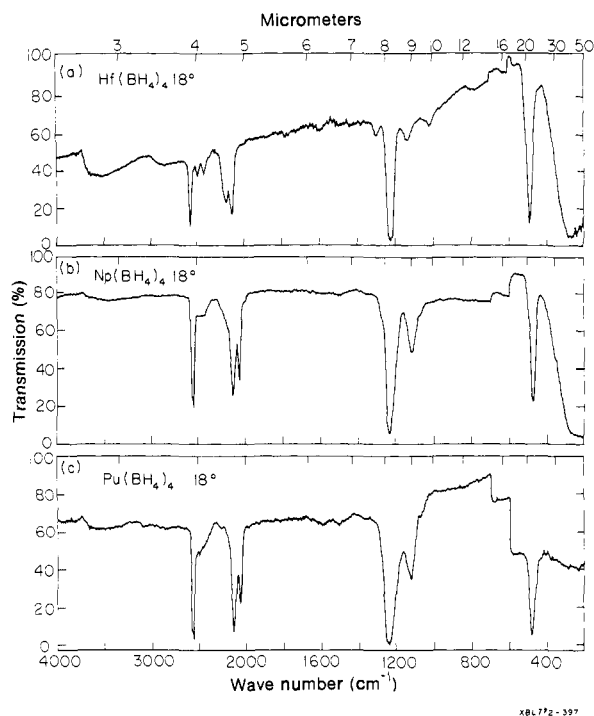
Figure 1. Gas phase infrared spectra of metal borohydrides.

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 $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ are moved to $\frac{1}{2},\frac{1}{2},0$.

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

Our preliminary Raman spectrum on solid $Np(BH_4)_4$ at -85 °C 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]

The physical properties of the known actinide(IV) borohydrides are summarized in Table I.

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

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Synthesis, Structure, and Spectral Properties of $(TFF)(HgCl_3)$, an Unusual Metallotetrathiaethylene

Sir:

Extensive investigations into the chemical and physical properties of low-dimensional organic materials have identified tetrathiafulvalene (TFF) as one of the major components of such systems. These materials are currently of great interest because of the demonstration of the existence of a one-dimensional metallic state.[1,2]

While there have been numerous studies devoted to purely organic charge-transfer salts, of which $(TFF)(TCNQ)$ is exemplary, considerably less attention has centered on inorganic salts of TTF.[3-5]

We report here the preparation and characterization of the trichloromercurate(II) salt of the TTF cation radical, $(TTF)(HgCl_3)$, **1**. In this solid, we observe three independent TTF cation radials, one having only C_1 crystallographic symmetry and two others with their centroids coincident with crystallographic centers of symmetry. Further, there are two distinctive chloromercurate(II) species: one a dimeric edge-bridged bitetrahedron $((HgCl_3)_2^{2-})$ and the other a polymeric species $((HgCl_3)_n^{n-})$ in which the coordination geometry is best described as trigonal bipyramidal.

Oxidation of tetrathiafulvalene with mercuric chloride in acetonitrile produced **1** and Hg_2Cl_2. Black, lustrous crystals were obtained from acetonitrile. Crystal data: $a = 12.661$ (3), $b = 15.969$ (4), $c = 7.416$ (2) Å; $\alpha = 98.69$ (2), $\beta = 95.73$ (2), $\gamma = 120.01$ (2)°; $V = 1256.2$ Å^3; $Z = 4$ (for $(TTF)(HgCl_3)$), space group $P\bar{1}$. Intensity data for 4298 independent reflections were collected employing monochromated Mo Kα radiation and the θ–2θ scan technique. The data were corrected for the usual geometric factors as well as absorption effects. The structure was solved by Patterson and Fourier methods and has been refined by the least-squares technique (anisotropic refinement for the nonhydrogen atoms and inclusion, but no refinement of the hydrogen atoms) to a final R_F value of 0.08.

Some aspects of the structure of $(TTF)(HgCl_3)$ are illustrated in Figure 1. Qualitatively, the structure can be separated into two types of two-dimensional layers. One of these layers (centered about $y = 0.0$) contains both inorganic and organic polymers propagating along the crystallographic c axis, Figure 1. The covalent inorganic polymer contains roughly trigonal bipyramidal coordination about the Hg(II) with equatorial Hg–Cl bond lengths ranging from 2.374 (5) to 2.545 (5) Å. The two axial bond lengths are considerably longer at 2.982 (5) and 3.112 (5) Å. The structural repeat unit is $HgCl_3^-$ with both axial ligands also involved in equatorial interactions. Colinear with this covalent inorganic polymer is a columnar array of TTF$^+$ radical cations, Figure 1. The molecular overlap