or may simply begin to participate in the cis–trans equilibration which dominates the cmr and pmr spectra at temperatures above −25°. The large 1450-Hz spectral range over which the resonances are spread causes no signals to be seen at −12°.

We find no other cmr signals which might correspond to the intermediate **5**. A recent cmr study[15] of over 20 $(h^5\text{-}C_5H_5)Fe(CO)_2X$ derivatives, where X represents a wide variety of substituents, showed that all CO resonances lie within 7.2 ppm of $Fe(CO)_5$, thus assuring that the signal at −50.2 ppm is not from **5**.

Studies of $Fe_3(CO)_{12}$ by cmr have been limited by solubility to a −10 to 50° temperature range. Only one sharp resonance is measured at −20.1 ppm *vs.* CS_2, whereas the crystal structure[16] has both bridging and terminal carbonyls, indicating that this molecule is either a triangle of iron atoms with each iron being bonded to four carbonyls or a fluxional molecule undergoing some sort of bridging-terminal CO interconversion of the type discussed above. Our research group has also obtained spectra at −110° for $Fe(CO)_5$, $[(C_6H_5)_3P]Fe(CO)_4$, and (norbornadiene)$Fe(CO)_3$. No structural interconversion was observed.

We are presently undertaking solvent dependent cmr studies of **1** as well as preparing the ^{13}C enriched dimer and $Fe_3(CO)_{12}$.

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[15] O. A. Gansow, D. A. Schexnayder, and B. Y. Kimura, *J. Amer. Chem. Soc.*, in press.

[16] C. H. Wei and L. F. Dahl, *ibid.*, **91**, 1351 (1969).

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Structure of Uranium Borohydride by Single-Crystal X-Ray Diffraction

Sir:

In conjunction with optical, vibrational, and magnetic resonance studies of metal tetrahydroborate complexes currently in progress in our laboratories, the need for detailed structural information about $M(BH_4)_4$ compounds (M = Zr, Hf, Th, U)[1] became apparent. Although X-ray diffraction results are available for $Zr(BH_4)_4$ at −160°, the exact positions of the bridging hydrogen atoms were not elucidated.[2] Thus neutron diffraction work appeared necessary to resolve this point and a program to study $M(BH_4)_4$ molecules using this technique was set up.[3] To prepare for these studies, the single-crystal X-ray structure of uranium borohydride was determined. The results are sufficiently interesting that, although lacking information about the hydrogen atom positions and subject to refinement following the neutron investigation, preliminary communication seems warranted.

Uranium borohydride, $U(BH_4)_4$, was synthesized from uranium tetrafluoride and aluminum borohydride according to the method of Schlessinger and Brown.[4] Dark green crystals suitable for X-ray diffraction were grown by vacuum sublimation and sealed in capillaries under nitrogen. An irregular plate of approximate dimensions 0.07 × 0.20 × 0.25 mm was used for data collection. Precession photographs revealed the Laue symmetry to be tetragonal, $4/mmm$, with the extinctions $h00$, $h \neq 2n$, and $00l$, $l \neq 4n$, consistent with the enantiomorphic pair of space groups $P4_12_12$ (No. 92) and $P4_32_12$ (No. 96).[5] The unit cell parameters are $a = 7.49 \pm 0.01$ Å and $c = 13.24 \pm 0.01$ Å, and assuming four formula weights per unit cell the calculated density of 2.66 g cm^{-3} seems reasonable.[6] A total of 560 independent hkl reflections[9] was collected by diffractometer using Mo Kα radiation at 20°. The data were corrected for background, Lorentz, polarization, and absorption ($\mu = 207.9$ cm^{-1}) effects. The structure was initially solved for the positions of the uranium and one boron atom from a three-dimensional Patterson map in space group $P4_12_12$.[9] The uranium atom occupies special position (4a) of site symmetry 2. A difference Fourier synthesis clearly revealed the position of the other crystallographically independent boron atom. Least-squares refinement of the atomic coordinates, anisotropic uranium atom thermal parameters, and isotropic boron thermal parameters converged at a value of 0.040 for the discrepancy index $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ based on 493 data points for which $I_{obsd} > 3\sigma(I_{obsd})$ and 14 variable parameters. The results are summarized in Table I and Figures 1 and 2.[11]

From Figure 1 it is readily apparent that the structure of uranium borohydride is polymeric, consisting of interlocking helical chains in which individual units are related by a fourfold screw axis. There are six tetrahydroborate groups associated with each uranium atom,

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[1] For a recent review of this class of compounds, see B. D. James and M. G. H. Wallbridge, *Progr. Inorg. Chem.*, **11**, 99 (1970).

[2] P. H. Bird and M. R. Churchill, *Chem. Commun.*, 403 (1967).

[3] Neutron diffraction studies are being carried out at the Brookhaven National Laboratories in collaboration with W. C. Hamilton and S. J. LaPlaca on uranium borohydride, and with the additional collaboration of W. J. Kennelly and T. J. Marks on hafnium borohydride.

[4] H. I. Schlessinger and H. C. Brown, *J. Amer. Chem. Soc.*, **75**, 219 (1953).

[5] "International Tables for X-Ray Crystallography," Vol. I, 3rd ed, Kynoch Press, Birmingham, England, 1969, pp 182, 186.

[6] The unit cell of uranium borohydride has been previously investigated by Zachariasen[7] and apparently mistakenly reported to be orthorhombic.[8] The original crystal class and unit cell parameters[7] are consistent with the present results. We thank Dr. Zachariasen for pointing out ref 7 to us.

[7] W. H. Zachariasen, Manhattan Project, Chicago Metallurigal Laboratory, CP 3774, July 1–Dec 1, 1946, p 17.

[8] H. R. Hoekstra and J. J. Katz, U. S. Atomic Energy Commission, AECD 1894, March 1948.

[9] Because of anomalous dispersion effects,[10] $F(hkl) \neq F(khl)$, and both forms of data were included in all calculations reported here. Trial refinements in both space groups (inverting the coordinates through the origin) indicated No. 96 to be the correct one, the final weighted and unweighted residuals being 0.050 and 0.041, respectively, in $P4_12_12$, compared to 0.048 and 0.040 in $P4_32_12$. All results reported here are for refinement in $P4_32_12$, in which the agreement between observed and calculated values of $|F(hkl)| - |F(khl)|$ after the final refinement was superior.

[10] J. A. Ibers, *Acta Crystallogr.*, **22**, 604 (1967), and references cited therein.

[11] A list of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-2552. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Table I. Atom Positional and Thermal Parameters for $U(BH_4)_4$[a]

Atom	x	y	z	β_{11}[b] or B[c]	β_{33}	β_{12}	β_{13}
U	−0.06953 (8)	−0.06953 (8)	0.0	58.6 (8)	14.2 (5)	−6 (1)	−1.6 (7)
B_b (bridging)	−0.211 (4)	−0.349 (3)	−0.126 (2)	2.6 (4)			
B_t (terminal)	0.212 (4)	−0.078 (4)	−0.106 (2)	3.1 (4)			

[a] Standard deviations, in parentheses, occur in the last significant figure for each parameter. [b] The form of the anisotropic ellipsoid for uranium is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, with the following symmetry constraints on the parameters: $\beta_{11} = \beta_{22}$; $\beta_{23} = -\beta_{13}$. Values reported are $\times 10^4$. [c] Isotropic thermal parameters (in Å^2) were assigned to the boron atoms.

four of which are bridging and two of which (in a cis configuration) are terminal. The bridging borohydride groups lie midway between the uranium atoms with a mean U···B distance of 2.87 ± 0.03 Å, significantly longer than the terminal U···B distance of 2.53 (3) Å (Figure 2). This feature of the structure is analogous to the pattern of Be···B distances in solid beryllium borohydride,[12] a helical polymer which is strikingly similar to uranium borohydride. The uranium–boron distances may be compared to the sum of the U and B atomic radii, 2.60 Å, tabulated by Slater.[13]

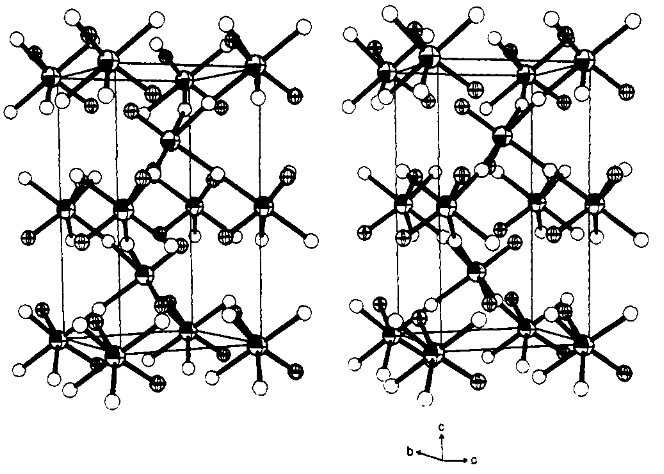

Figure 1. Stereoscopic unit cell packing diagram for $U(BH_4)_4$. Fourfold screw axes parallel to c intersect the ab plane at ($^1/_2$, 0) and (0, $^1/_2$). Lines connecting the uranium (large spheres) and boron atoms are drawn to illustrate the U–BH$_4$ connectivity and are not meant to imply direct U–B bonding.

Although a definitive assessment of the coordination geometry of individual uranium atoms must await completion of the neutron diffraction work, it is possible that each uranium atom is bonded to six tetrahydroborate groups through two, three-center U–H–B bonds,[14] resulting in a formal coordination number of 12. It is interesting in this respect that in β-uranium hydride, UH_3, the uranium atoms are also dodecacoordinate.[16] Both icosahedral (T_h symmetry) and truncated tetrahedral (T_d symmetry) coordination polyhedra[17] exist in the β-uranium hydride structure. An icosahedral coordination polyhedron for $U(BH_4)_4$ and a truncated tetrahedral geometry for $Zr(BH_4)_4$ would not be inconsistent with the X-ray structural information (Figure 2 and ref 2), and it remains to be seen whether these expectations will be fulfilled.

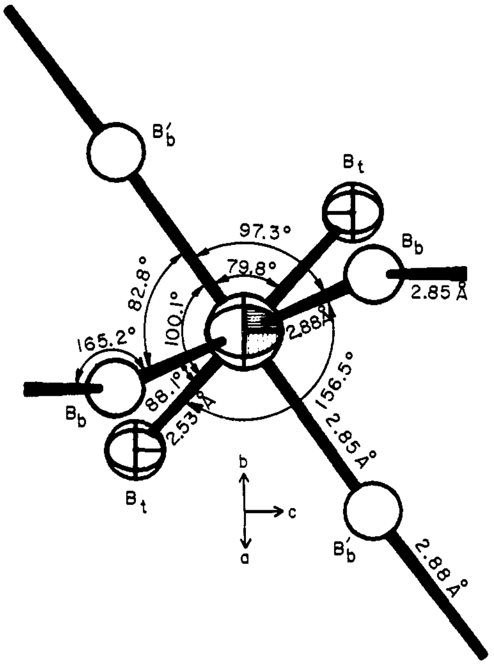

Figure 2. Site symmetry of $U(BH_4)_4$ viewed down the crystallographically imposed C_2 axis. Standard deviations in U–B bonds are ±0.03 Å, in B–U–B angles, ±0.8°, and in the U–B–U angle, ±1.0°. Angles not shown are B_t–U–B_t, 110.4°, B_b'–U–B_b', 179.8° and B_b–U–B_b, 78.7°.

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(12) D. S. Marynick and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **93**, 2322 (1971).

(13) J. C. Slater, *J. Chem. Phys.*, **41**, 3199 (1964).

(14) A two-point attachment of tetrahydroborate ligands has been established for $Be(BH_4)_2$,[12] $(CH_3)_3NAl(BH_4)_3$,[15a] $[(C_6H_5)_3P]_2Cu(BH_4)$,[15b] and $(h^5\text{-}C_5H_5)_2Ti(BH_4)$.[15c]

(15) (a) N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, *Inorg. Chem.*, 7, 1575 (1968); (b) S. J. Lippard and K. M. Melmed, *ibid.*, **6**, 2223 (1967); (c) K. M. Melmed, Ph.D. Thesis, Columbia University, 1971.

(16) (a) R. E. Rundle, *J. Amer. Chem. Soc.*, 73, 4172 (1951); (b) R. N. R. Mulford, F. E. Ellinger, and W. H. Zachariasen, *ibid.*, **76**, 297 (1954).

(17) For a discussion of dodecacoordinate geometries, see E. L. Muetterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, 21, 109 (1967).

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