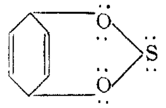
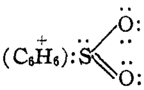
the plane of the ring rather than one[7b,c] in which the axis of the halogen molecule is coincident with the sixfold symmetry axis of the ring. His preference is based on group theory-symmetry considerations and on the argument that van der Waals forces will be greater for the more compact model. For the benzene–silver ion complex similar considerations as based on group theory lead Mulliken to the conclusion that the most favorable location for silver ion is off the six-fold symmetry axis of the ring.[14,16] This conclusion is borne out by preliminary interpretation of X-ray crystallographic measurements of $AgClO_4 \cdot C_6H_6$.[18]

In considering the question of the relative configurations in space of the two molecules contributing to the sulfur dioxide complex two structural types patterned after those discussed previously and in keeping with the non-linear structure of the inorganic component of the complex[19] are sufficiently interesting to deserve specific mention. The first is spatially similar to that proposed by Mulliken for the iodine complex[17] and involves an O–S–O bridge between para positions of the ring with the center of the sulfur atom on a line through the center and perpendicular to the plane of the ring.



One would suspect, however, that the sulfur rather than the oxygen atoms resides nearest the aromatic nucleus in the complex.[20] A structure in which the sulfur dioxide molecule again lies above the plane of the ring but with the sulfur atom making the closest approach to that plane seems preferable. Small contributions from ionic forms such as  would contribute to the stability of such a complex.

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[18] Rundle and Goring, THIS JOURNAL, **72**, 5337 (1950).

[19] See for example Schomaker and Stevenson, *ibid.*, **62**, 1270 (1940).

[20] This reasoning is in keeping with the observation that conjugated dienes react with sulfur dioxide to form cyclic sulfones. Grummitt, Ardis and Fick, *ibid.*, **72**, 5167 (1950), present a discussion of the mechanism of this reaction which is of considerable interest in relation to the results of the present study.

[CONTRIBUTION NO. 73 FROM THE INSTITUTE FOR ATOMIC RESEARCH, IOWA STATE COLLEGE]

The Hydrogen Positions in Uranium Hydride by Neutron Diffraction[1]

BY R. E. RUNDLE

The hydrogen positions in UD_3 have been determined by neutron diffraction, showing that the bridge structure previously proposed is incorrect. The hydrogens lie in distorted tetrahedra, equidistant from four uranium atoms, with U–D = 2.32 A. There are two types of uranium atoms in the structure, each with twelve nearest D atoms at this distance. The structure is illustrated.

Introduction

Uranium hydride, UH_3, has a primitive cubic lattice, a_0 = 6.63 kX., and a metal arrangement like that of β-tungsten, *i.e.*, $2U_I$ at 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $6U_{II}$ at $\pm\frac{1}{4}0\frac{1}{2}\circlearrowleft$.[2] It has been suggested that the hydrogen atoms lie at the midpoints of the ligands between U_I and U_{II}, so that the hydrogen atom would form two interatomic links to uranium, presumably with one electron pair.[2] In support of the above structure Pauling and Ewing[3] pointed out that the U–H distances given by the proposed structure are in excellent agreement with those calculated from Pauling's rule and metallic radii.[4]

Structures in which hydrogen bridges two atoms together with one electron pair have become quite popular as explanations of electron deficient bonding. The cases where this type of bonding has been verified experimentally are, however, still very few in number, and none of the verified cases include metallic hydrides. For several reasons it seemed important to check the proposed structure of UH_3. This is possible only by neutron diffraction.

Because of the higher coherent scattering factor and lower spin diffuse scattering of deuterium for neutrons,[5] UD_3 rather than UH_3 was used for neutron diffraction study. The results show without question that the suggested bridge structure is incorrect, and provide a different and more complex structure for the hydride.

Structure Determination

Preparation of the Deuteride.—UD_3 was made from uranium metal and deuterium gas. D_2 was prepared from D_2O by Newton's method,[6] which in the final step involves decomposition of UD_3, and furnishes deuterium very free of oxygen, carbon and nitrogen. The D_2O, furnished by the A. E. C., contained less than 0.2% of the hydrogen as H.

Neutron Diffraction Data.—The powder diffraction data (Fig. 1) were obtained by C. G. Shull using the apparatus and method described by Wollan and Shull.[5] Integration across the diffraction maxima, (*hkl*), gives the power, P_{hkl},

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[1] Presented in part at the Am. Chem. Soc. Convention, San Francisco, Calif., April, 1949.

[2] R. Rundle, THIS JOURNAL, **69**, 1719 (1947).

[3] L. Pauling and F. J. Ewing, *ibid.*, **70**, 1660 (1948).

[4] L. Pauling, *ibid.*, **69**, 542 (1947).

[5] E. O. Wollan and C. G. Shull, *Phys. Rev.*, **73**, 830 (1948).

[6] F. Spedding, A. Newton, J. Warf, O. Johnson, R. Nottorf, I. Johns and A. Daane, *Nucleonics*, **4**, 4 (1949).

for this Bragg reflection (Table I). In this case all apparatus constants were known from previous work, so that P_{hkl} is absolute power in neutrons/min.

Prior to this work the coherent scattering factor for uranium was unknown. This was determined for a wave length of 1.057 Å. by a study of UC and UO_2, leading to the value $f_U = 0.85 \times 10^{-12}$ cm., $\sigma_U = 8.7$ barns.[7] The scattering factor used for deuterium, $f_D = 0.64 \times 10^{-12}$, was a revised value obtained from a study of ThD_2 and other deuterides.[7]

Positions Available for Hydrogen Atoms.—The uranium positions in UH_3 are provided by five cubic space groups, O_h^3-Pm3n, O^2-$P4_23$, T_d^4-P43n, T_h^1-Pm3 and T^1-P23. In the latter two space groups the 6-fold positions for U_{II} involve one parameter, which would then be exactly $^1/_4$.

There are 24 hydrogens per unit cell. The 24-fold sets available are

From O_h^3-24(j), involving one parameter
-24(k), involving two parameters
From O^2-24(m), a general set
From T_d^4-24(l), a general set
From T_h^1-24(l), a general set

Very simple intensity considerations eliminated the set 24(j) from O_h^3. The set, 24(k), with $y \cong 0.150$, $z \cong 0.30$ appeared promising. Considering only reflections ($hk0$), the 24-fold sets from O^2 and T_d^4 have identical structure factors and led to the same set of parameters, $x = 0.06$, $y = 0.15$, $z = 0.30$, or an equivalent set at $\bar{x}\bar{y}\bar{z}$. In both cases, however, the structures so derived were unsatisfactory for general reflections, (hkl). The set 24(l) of T_h^1 was eliminated by consideration of the simplest reflections, *e.g.*, the reflections (00l) and (001) alone eliminated this possibility. Since 24(k) of O_h^3 appeared to make the ratio, (023):(231) rather low, see below, we spent some time attempting to find another satisfactory structure. It was found possible to eliminate combinations of 12-, 16- and 8-fold sets from O_h^3, O^2 and T_d^4. Preliminary work indicated that it would be difficult to explain the absence of all reflections (hhl) with l odd using the 12-fold sets of T_h^1 and T^1. A complete study of these possibilities was not made.

The original estimate of the ratio (023):(231), was about 5:1. Using set 24(k) it was impossible to achieve anything like this great a ratio while keeping (200) small. For this reason a random structure based on 48(l) of O_h^3 was examined. This gave for x, y and z, values of 0.04, 0.14 and 0.29, respectively, and amounted to splitting each position in 24(k) into two positions about 0.5 Å. apart. Though this is a possibility, it is now thought the graphical resolution of the (023), (231) peak probably gave too great a ratio. If a ratio of 2:1 is accepted, and this does not appear to be excluded by the shape of the peak, then positions in 24(k) can be found which are in better overall agreement with observed intensities than anything which can be achieved if the (023):(231) ratio is made to approach 5.

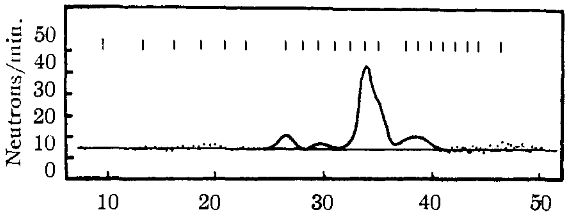

Fig. 1.—Neutron scattering curve for UD_3; wave length 1.057 Å.; lines above the curve indicate position of the expected maxima.

A variation of parameters was carried out, and the best that can be found for 24(k) is $y = 0.155 \pm 0.02$, $z = 0.31 \pm 0.02$. This is sufficiently close to $y = 0.156$, $z = 0.313$, which puts each hydrogen atom equidistant from four uranium neighbors, to suggest that the hydrogen is so located.

The above structure gives satisfactory agreement between calculated and observed neutron intensities (Table I). For calculation of intensities the formula

$$P_{hkl} = \frac{kP_0\,\rho' j_{hkl}\,N^2F^2_{hkl}}{\rho \sin^2 2\theta}$$

was used where P_0 is the power in the incident beam, j_{hkl} is the multiplicity factor, ρ' is the density of the powder, ρ is the crystal density, N is the number of unit cells/cc., F_{hkl} is the structure factor for neutrons and $\sin^2 2\theta$ is the Lorentz factor for the block powder procedure employed. No temperature correction was made. The apparatus constant, k, was known, so that absolute agreement as well as the ratio of intensities is significant.

TABLE I

NEUTRON DIFFRACTION POWDER DATA FOR UD_3

Indices	$P_{obsd.}$	$P_{calcd.}$ New structure	$P_{calcd.}$ Bridge structure
100	0	0	0
011	0	1	166
111	0	0	0
002	Visible ?	34	42
021		2	67
211	0	10	28
022	120	71	87
(221) (300)	0	0	0
013	57	44	0
311	0	0	0
222	0	1	10
023	840	720	28
123		327	101
400	200	70	132
(401) (322)		100, 0	0
(411) (033)		0, 48	15
(402)	0	0	
421	0	14	
(233)	0	0	
(422)	Visible ?	48	

Included in Table I are calculated intensities for the bridge model previously proposed.[2] It is to be noted that hydrogen atoms in the "ideal" bridge structure would be in 24(k) of O_h^3 with $y = {}^1/_4$, $z = {}^1/_8$. The derived structure comes close

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(7) C. G. Shull, private communication.

to being an interchange of y and z. Such an interchange changes the sign of the hydrogen contributions of all reflections with $(h + k + l) = 2n + 1$, and, among other things, makes (023) very weak, whereas it is observed as the strongest reflection from the deuteride. There is no possibility of a slightly deformed bridge structure.

Discussion

The structure is illustrated in Fig. 2. The hydrogen atoms are in the center of a deformed tetrahedron, and, as nearly as can be determined, they are equidistant from four uranium neighbors. The U–D distance is 2.32 Å. Thus the hydrogen is in an enormous hole if our notions about radii apply to metallic hydrides. Pauling gives as the radius of uranium for coördination number twelve, 1.52 Å. The "radius" for hydrogen then appears to be 0.80 Å., or three times the "normal" radius.

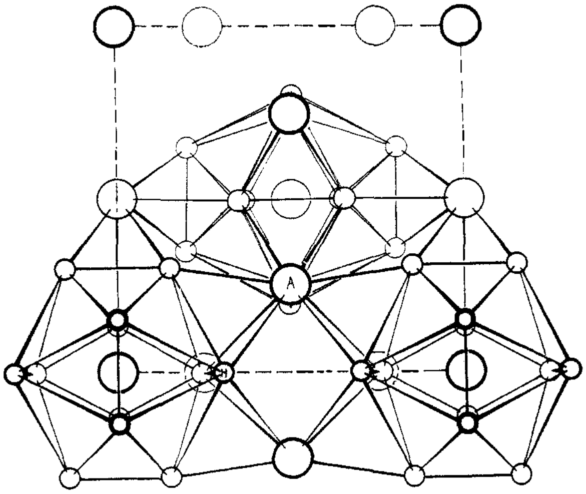

Fig. 2.—Partial drawing of the structure of UD_3. Icosahedra of deuterium atoms (small circles) surround $U_{\rm I}$ atoms at corners and center of cube. Coördination about $U_{\rm II}$ is best illustrative by atom A which is shown bonded to one face of each of three icosahedra. Another is above the icosahedron at the center of the cube, also bonded to A. The configuration about the hydrogens can be seen from atom H, above the plane. There is one $U_{\rm I}$ atom and two $U_{\rm II}$ atoms at $^1/_2, ^1/_4, 0$ and $^1/_2, -^1/_4, 0$. The fourth $U_{\rm II}$ atom about H is almost directly above H, making four U atoms about H in a distorted tetrahedron.

As pointed out earlier,[2] almost no metallic U–U bonds of importance are left in the structure. Consequently, one must assume that the structure is held together principally by uranium–hydrogen interactions. The hydride is not saline, but metallic, so these interactions are presumably best described in terms of delocalized covalent bonds.

Each $U_{\rm I}$ atom is surrounded by twelve hydrogen atoms at the corners of an icosahedron of symmetry T_h. (This is not the regular icosahedron but has isosceles rather than equilateral triangles for twelve of the twenty faces.) All hydrogens are equidistant from the uranium atom.

$U_{\rm II}$ atoms also are surrounded by twelve hydrogens, but in sets of three, each set forming a face of a different icosahedron. The configuration about $U_{\rm II}$ is essentially that of a truncated tetrahedron, and the $U_{\rm II}$ atoms bind the icosahedra together (Fig. 2). The $U_{\rm II}$–D distances are equal to $U_{\rm I}$–D distances. Consequently, in this structure the metallic valence, as defined by Pauling,[4] is about equal for $U_{\rm I}$ and $U_{\rm II}$, though it was very different for the proposed bridge structure.[3] The chief difference between $U_{\rm I}$ and $U_{\rm II}$, is in the U–U bonding which is somewhat better for $U_{\rm II}$, each of which has two nearest $U_{\rm II}$ neighbors at 3.31 Å., a long bond, but one which would have a bond number of 0.16 by Pauling's rule.[4]

If Pauling's rule and radii ($R_{\rm U}(1) = 1.421$, $R_{\rm H}(1) = 0.30$ Å.) are applied to obtain the valence of uranium, one finds 1.7 for $U_{\rm I}$ and 1.8 for $U_{\rm II}$. These values seem so small that they must mean that Pauling's rule is not applicable. However, the idea that the uranium valence is smaller than in the metal is supported by the magnetic susceptibility of the hydride which Dr. R. F. Raeuchle has found to be greater than that of the metal.

The high susceptibility, which has not yet been examined thoroughly, may mean that uranium is tetravalent in the hydride, with two 5f electrons. A tetravalence for uranium would lead to 56 electrons/cell *versus* 53.5 needed to fill the Brillouin zone, as discussed by Pauling and Ewing.[3] If we make the reasonable assumption that the four U–D bonds about each D atom have bond number 0.25, instead of 0.1 as calculated by Pauling's rule, then the U–D contribution to the valence of uranium is three. Metal–metal bonds would increase the valence somewhat, so again, a metallic valence of four is reasonable for both $U_{\rm I}$ and $U_{\rm II}$.

As noted earlier, the deuterium atoms are found in holes that are far larger than they would seem to require. Since a very great expansion of uranium takes place upon forming the hydride, one cannot attribute the long U–D bonds to the filling of pre-existing holes which happen to be too large. The holes for hydrogen are created by formation of the hydride. Neither can it be argued that the long U–D bonds mean a weak uranium–hydrogen interaction. UH_3 is formed with a considerable evolution of heat; ΔH formation $= -30.8$ kcal./mole,[6] even though formation of the hydride involves the breaking of H–H bonds, and the lengthening of all U–U bonds. It appears that something else is required before metal–hydrogen distances in heavy metal hydrides are well understood.

Acknowledgment.—This investigation could not have been carried out without the very considerable assistance of Dr. C. G. Shull of the Oak Ridge National Laboratory, who secured the neutron diffraction data and the required neutron scattering factors. We are also indebted to both Dr. E. R. Wollan and Dr. Shull for advice during the structure investigation. Dr. R. F. Raeuchle prepared the deuteride.

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