configurations should be equally occupied; this is consistent with our observation that the refined temperature parameters for the alternative methylene sites are very nearly equal. For type ii, which lies on the $\bar{4}$ site, there is evidence from the thermal parameters that the two configurations may not be equally occupied. In the absence of crystal forces, type ii represents a more energetically favorable state for the tetraethylammonium ion than type i, in that the average distance between methyl groups is the greater.

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The Crystal Structure of Aluminum Hydride[1]

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X-Ray and neutron powder diffraction data for aluminum hydride, AlH_3, and aluminum deuteride, AlD_3, were used to solve this structure. Both compounds crystallize in the trigonal space group $R\bar{3}c$ with six molecules in a hexagonal unit cell of dimensions $a = 4.449$ Å and $c = 11.804$ Å for the hydride and $a = 4.431$ Å and $c = 11.774$ Å for the deuteride. Least-squares refinement of this three-parameter problem using seven unique AlD_3 neutron powder diffraction peaks gave a final R_1 of 0.026. The refined parameters gave $R_1 = 0.040$ for 29 AlH_3 X-ray powder diffraction peaks. Columns of Al atoms and spirals of H atoms are parallel with the c axis and are packed so that the Al has octahedral coordination symmetry. The final $\mathrm{Al}\cdots\mathrm{H}$ distance of 1.72 Å, the participation of each Al in six bridges, and the equivalence of all $\mathrm{Al}\cdots\mathrm{H}$ distances suggest that 3c–2e bonding occurs. The closest Al–Al distance is 3.24 Å. The alternating planes of Al and H atoms, perpendicular to the c axis, result in a stable structure which is a three-dimensional network of $\mathrm{Al}\cdots\mathrm{H}\cdots\mathrm{Al}$ bridges and is consistent with the observed high density of the crystal.

The existence of four aluminum hydrides has been reported in the literature. AlH is a short-lived species produced by an electrical discharge between electrodes[2] and has been used to provide a measurement of the Al–H bond length (1.648 Å). The preparation of a polymerized hydride $(AlH_3)_n$ has been claimed by Stecher and Wiberg,[3] but Finholt, Bond, and Schlesinger[4] reported that method to be difficult, giving a somewhat impure product. Their preparation used $LiAlH_4$ and $AlCl_3$ in ether to give a pure product but one from which the ether could not be removed without causing decomposition. Some recent work here at Dow has resulted in five crystalline forms of nonsolvated aluminum hydride.[5] One of these, designated as pattern 1433 in our files, has been reported by two other groups of workers—Rice and Chizinsky,[6] who precipitated it from pentane, and Appel and Frankel,[7] who produced it by bombarding an ultrapure aluminum target with hydrogen ions. However, the X-ray data taken by this second group were of too poor a quality to make the identification unique. In particular, the least-squares fit to a hexagonal unit cell seems to indicate the possibility that their product corresponds to our pattern 1451. Finally, Breisacher and Siegel[8] prepared gaseous AlH_3 and its dimer in a flow system by evaporating aluminum from a hot tungsten filament into hydrogen at low pressure. In a similar experiment, using a static system, the product was trapped out at −195°.[9]

Aluminum does not form a low molecular weight hydride analogous to the simple dimeric hydrides of boron and gallium, and there has been speculation[3,10,11] on the molecular structure of $(AlH_3)_n$ since its first preparation, with all of the proposed structures suggesting that hydrogen bridging is required. Some extended Hückel calculations done by Kato, *et al.*,[12] using a symmetry of C_{3v} and a bond distance of 1.65 Å for AlH_3, lead to an interpretation of the bonding in the structure as having partial ionic character which might be represented as $\mathrm{Al}^{+\delta}\cdots\mathrm{H}^{-\delta}$. Infrared spectroscopy studies[13] led Roszinski, *et al.*, to describe $(AlH_3)_n$ as having a branched and cross-linked structure with

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only H bridges and no terminal hydrogens and with Al having a coordination number of 6. The work reported here was undertaken to establish the crystal structure of an aluminum hydride and to investigate the nature of the bonding involving the hydrogen. Of the five forms available, 1451 is the most stable and it was chosen for our study.

Experimental Section

Unit Cell Refinement.—The sample used was a fine, white, crystalline powder with an average crystallite size of 5 μ, too small for single-crystal work. Elemental analysis showed the material to be solvent free. On exposure to air, a fine, white powder formed on the crystal surfaces, but no changes in the diffraction patterns were observed. Subsequent exposures showed the material to be stable in air with no further deterioration

Initial Debye–Scherrer powder patterns for AlH_3 were indexed on the basis of a hexagonal unit cell of dimensions $a = 4.455$ Å and $c = 5.911$ Å, by analogy with the powder pattern for tellurium to which the hydride pattern shows a striking resemblance. Subsequently, powder data taken with crystal-monochromatized Cu Kα_1 (1.54050 Å) radiation on an AEG (Allgemeine Electrizitats-Gesellschaft) Guinier camera using Seeman–Bohlin focusing[14] were used with the method of axial ratios[15] to refine the initial unit cell. A 7.5-μ Al foil used as the sample holder provided reference lines. During the refinement it became apparent that one weak line which could not be indexed with the original unit cell but which was known to belong to the pattern would fit nicely (indexed as 113) if the z axis were doubled. This was done giving final unit cell dimensions of $a = 4.4493 \pm 0.0005$ Å and $c = 11.8037 \pm 0.0024$ Å for hexagonal axes, corresponding to $a = 4.699$ Å and $\alpha = 56.52°$ for the rhombohedral cell. The calculated density of 1.4768 g/cm^3 agrees well with the value of 1.477 ± 0.005 g/cm^3 measured with a Beckman Model 930 air comparison pycnometer.

The AlD_3 unit cell refinement also used data taken on the AEG camera and the method of axial ratios. Final unit cell dimensions are $a = 4.4309 \pm 0.0005$ Å and $c = 11.7744 \pm 0.0006$ Å, and the corresponding rhombohedral cell has the dimensions $a = 4.685$ Å and $\alpha = 56.45°$. The calculated density is 1.4928 g/cm^3.

Space Group.—Work was begun assuming space group $P3_121$ (*hkl:* no conditions; *00l:* $l = 3n$) as in the tellurium structure. Subsequently, Duke, *et al.*,[16] were able to determine the Laue group as $\bar{3}$m and the lattice as rhombohedral from single-crystal Weissenberg photographs taken with a 7-μ fragment. They gave R32, R3m, and $R\bar{3}m$ (*hkl:* $-h + k + l = 3n$) as possible space groups with a unit cell of dimensions $a = 4.455$ Å and $c = 5.911$ Å. Our data set of 27 X-ray powder diffraction lines could be indexed assuming space group $R\bar{3}c$ (*hkl:* $-h + k + l = 3n$; *h0l:* $l = 2n$) and we have assigned this space group to the structure. Duke's three possible space groups required two sets of special positions or a set with a variable z coordinate to describe the positions of the six aluminum atoms (which we have assigned to special position 0, 0, 0; 0, 0, $^1/_2$ [0, 0, 0; $^1/_3$, $^2/_3$, $^2/_3$; $^2/_3$, $^1/_3$, $^1/_3$] +) in the unit cell. The absence of any physical data indicating two types of aluminum atoms and the good fit of observed and calculated data with aluminum in the positions given above support the choice of the higher symmetry space group. It is also of interest to note that $R\bar{3}c$ is the space group of choice for most of the trifluorides with which the AlH_3 is isostructural.[17]

Diffraction Data.—X-Ray powder diffraction data for the hydride were taken on a Norelco diffractometer with a xenon-filled proportional counter and strip chart recorder. Ni-filtered Cu Kα (1.5418 Å) radiation was used for 2θ scans taken at a scan rate of 2°/min. Peak heights above background were read from seven scans taken with two different samples and four different sets of scaling constants. After scaling and averaging, the data were converted to integrated intensities using conversion factors determined by Swanson, *et al.*[18] Corrections for Lorentz-polarization and multiplicity factors were made giving a final set of 27 structure factors.

Neutron powder diffraction data for the deuteride were taken at Argonne National Laboratory through the courtesy of the late Dr. S. S. Sidhu. Neutrons of wavelength 1.069 Å were used with a 0.1° 2θ step–scan technique to collect data over the range $10.0° \leqslant 2\theta \leqslant 98.0°$. Plotting counts *vs.* 2θ showed 19 resolved peaks which were graphically integrated using a planimeter. Seven of these peaks could be indexed uniquely.

Structure Determination.—Working in hexagonal coordinates in space group $R\bar{3}c$ the 6 Al atoms can be in special positions 6(a) or 6(b) and the 18 H atoms in special positions 18(d) or 18(e). From packing considerations, Al in 6(a) requires H in 18(d) and Al in 6(b) requires 18(e). Structure factor calculations for the deuteride neutron data using scattering lengths $b_{Al} = 0.35$ and $b_D = 0.65$[19] showed the 6(b)–18(e) combination to be the correct one. Deuteride neutron diffraction intensity ratios for a set of six uniquely indexed peaks were used with expanded structure factor expressions to give a polynomial in x, the position parameter for deuterium. The solution of the polynomial gave a value for x which was then refined by least squares on neutron data for seven reflections [minimizing $\Sigma(F_o - F_c)^2$]. The refined value of x and starting thermal parameters of 1.0 for both atoms were used with the X-ray data to determine thermal parameters for the hydride.[20,21] One cycle gave 0.93 Å^2 for Al and -3.34 Å^2 for H indicating that the X-ray data are not of high enough quality to allow such a refinement. Alternatively, the atomic scattering factor used for hydrogen may be ill suited to this structure in which the hydrogen may well have considerable ionic character. However, in view of the unreliability of X-ray data in solving questions of this sort, no conclusions are drawn here. Final atomic parameters are given in Table I. The reliability indices are given by the expressions $R_1 = \Sigma|F_o - F_c|/\Sigma|F_o|$ and $R_2 = \{\Sigma[F_o - F_c]^2/\Sigma[F_o]^2\}^{1/2}$. Table II lists observed and calculated structure factors for the hydride and the deuteride, Table III compares observed and calculated intensities for the deuteride neutron data, and Table IV gives all bond distances and angles.

Results and Discussion

The structure comprises alternating planes of aluminum and hydrogen atoms stacked perpendicular to the z axis and spaced a distance $z/12 = 0.984$ Å apart, center to center (see Figure 1). Each aluminum is surrounded octahedrally by six hydrogens, three in the plane above and three in the plane below, and thereby participates in six three-center Al···H···Al bonds as shown in Figure 2. The Al–H (bridging) distance is 1.715 Å. This value lies between that given by the sum of the ionic radii, $r_{Al^{3+}} + r_{H^-} = 0.50 + 1.53 = 2.03$ Å, and that given by the sum of the covalent radii, $r_{Al} + r_H = 1.18 + 0.37 = 1.55$ Å.[22] It is shorter than

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Table I

Final Atomic Parameters and Reliability Indices

	AlH_3 (X-ray)		AlD_3 (neutron[a])	
	Al	H	Al	D
x	0.000	0.628	0.000	0.628 (2)
y	0.000	0.000	0.000	0.000
z	0.000	0.250	0.000	0.250
B	1.00	1.00	0.25 (55)	1.77 (43)
R_1 (obsd)	0.040	29 reflections	0.026	7 reflections
R_2 (obsd)	0.052		0.033	

[a] Numbers in parentheses are the estimated standard deviations as calculated from the variance–covariance matrix obtained in the final cycle of least-squares (×10^3 and ×10^2 for position and thermal parameters, respectively).

Table II

Observed and Calculated Structure Factors for Unique Reflections

AlH_3 - X-ray data

h	k	ℓ	Y(obs)	Y(calc)
0	1	2	43.02	46.18
1	0	4	39.05	38.70
1	1	0	36.03	35.59
0	0	6	29.64	31.04
1	1	3	5.85	4.34
2	0	2	32.28	33.68
0	2	4	37.49	33.82
1	1	6	34.05	32.18
1	2	2	30.15	29.69
0	1	8	30.64	28.75
2	1	4	27.93	27.80
3	0	0	29.25	29.23
2	0	8	24.89	25.51
1	0	10	23.92	24.16
2	2	0	22.33	23.00
0	3	6	21.20	21.45
3	1	2	20.75	22.37
1	2	8	20.93	21.55
0	2	10	19.61	20.33
1	3	4	20.26	20.27
0	0	12	23.45	21.04
2	2	6	18.59	19.85
0	4	2	19.00	19.24
1	1	12	17.25	16.92
2	3	2	16.49	16.17
3	1	8	16.32	15.99
3	2	4	15.75	15.88
4	1	0	14.67	15.21
0	1	14	16.69	15.03

AlD_3 - neutron data

h	k	ℓ	Y(obs)	Y(calc)
0	1	2	13.27	13.50
0	2	4	19.72	19.41
1	1	6	25.18	25.14
2	1	1	11.76	11.35
1	2	5	9.27	10.51
2	0	8	17.81	17.60
2	3	2	3.98	3.76

Table III

Observed and Calculated Neutron Diffraction Intensities for AlD_3

h	k	ℓ	I/I_1 (obs)	I/I_1 (calc)		2θ (obs)	2θ (calc)
0	1	2	18.34	20.15		18.98	19.14
1	0	4	7.93	0.41	7.48	27.80	26.46
1	1	0		7.07			27.92
0	0	6	100.00	14.42	100.00	32.03	31.61
1	1	3		85.58			32.17
0	2	4	10.66	10.88		38.84	38.85
1	1	6	29.42	30.89		42.68	42.68
2	1	1	6.19	6.06		43.58	43.59
1	2	2	3.51	2.61	2.83	44.26	44.61
0	1	8		0.22			45.78
2	1	4	27.87	2.46	27.31	49.42	48.51
3	0	0		24.85			49.40
1	2	5	2.91	3.94		51.52	51.29
2	0	8	4.87	5.01		54.60	54.48
1	1	9	27.17	20.10	25.13	56.80	56.65
1	0	10		2.08			56.70
2	2	0		0.19			57.70
2	1	7		2.76			58.24
0	3	6	40.31	4.40	30.68	60.40	59.84
2	2	3		12.24			60.18
1	3	1		4.73			60.56
3	1	2		7.74			61.37
1	2	8		1.57			62.32
0	0	12	17.02	5.17	19.03	67.09	66.02
3	1	5		3.51			66.89
2	2	6		7.22			67.29
0	4	2		3.13			68.74
2	1	10	3.98	1.16	4.65	73.18	71.57
4	0	4		0.02			71.75
1	3	7		2.69			72.93
1	1	12		0.50			73.14
3	2	1		0.28			75.01
2	3	2	0.31	0.29		75.90	75.74
3	1	8	13.49	0.00	12.99	78.81	76.60
1	2	11		1.19			76.72
2	2	9		5.43			78.43
3	2	4		6.35			78.65
4	1	0		0.02			79.33
2	3	5	6.69	0.22	3.97	81.71	80.81
0	1	14		0.99			81.18
1	4	3		2.76			81.49
0	4	8		0.00			83.38
1	3	10	11.63	3.58	14.48	87.45	85.22
3	2	7		0.18			86.52
0	3	12		5.58			86.72
2	0	14		0.00			87.88
1	4	6		3.76			87.89
2	1	13		0.76			88.18
5	0	2		0.62			89.23
2	3	8	9.52	4.58	25.03	92.45	90.06
3	1	11		1.36			90.18
4	0	10		1.60			91.89
0	5	4		4.17			92.06
1	1	15		4.40			92.51
3	3	0		2.66			92.73
2	2	12		0.00			93.39
1	2	14		0.81			94.56
3	3	3		0.08			94.86
2	4	1		2.46			95.20
1	0	16		0.18			95.39
4	2	2		2.73			95.91

the ionic value (2.1 Å) found for aluminum borohydride[23] in which the aluminum is also surrounded octahedrally by hydrogens, which are at a distance of 1.28 Å from boron, close to the covalent B–H distance of 1.19 Å. It is longer than that found for the short-lived species Al–H (1.648 Å)[2] and is much longer than the essentially covalent distance found in lithium aluminum hydride (1.547 Å)[24] in which each aluminum is tetrahedrally surrounded by hydrogens which are at a distance of 1.94 Å from the lithium atoms, close to the ionic Li–H distance of 2.04 Å. In the two structures aluminum borohydride and lithium aluminum hydride the hydrogens can be said to participate in conventional hydrogen bonding, while in our AlH_3 structure, the hydrogen participates in three-center 3c–2e bonds to form bridges between aluminum atoms.

Table IV

Interatomic Distances and Angles in AlH_3[a]

Distances, Å		Angles, deg	
Al(6)-H(7)	1.715	Al(6)-H(5)-Al(4)	141.2
H(7)-Al(8)	1.715	H(5)-Al(6)-H(7)	89.6
Al(6)-Al(8)	3.236	H(3)-H(7)-H(11)	172.5
Al(6)-Al(4)	3.236		
Al(6)-Al(6)	4.449	H(5)-H(7′)-H(5′)	60.4
Al(6)-Al(12)	5.902	H(7′)-H(5)-H(5)	59.8
		H(5′)-H(5)-H(7′)	59.8
H(5)-H(7)	2.418		
H(5)-H(7′)	2.418		
H(5)-H(7″)	2.587		
H(5)-H(3)	2.418		
H(5)-H(3′)	2.418		
H(5)-H(3″)	2.587		
H(5)-H(5′)	2.434		

[a] Numbers in parentheses refer to the *z* coordinates of the atoms, in twelfths of the unit cell dimension along *z* (see Figure 1). Errors in distances are approximately ±0.01 Å and in angles ±0.5° from the error in the *x* coordinate of hydrogen as computed from the variance–covariance matrix obtained in the final least-squares cycle.

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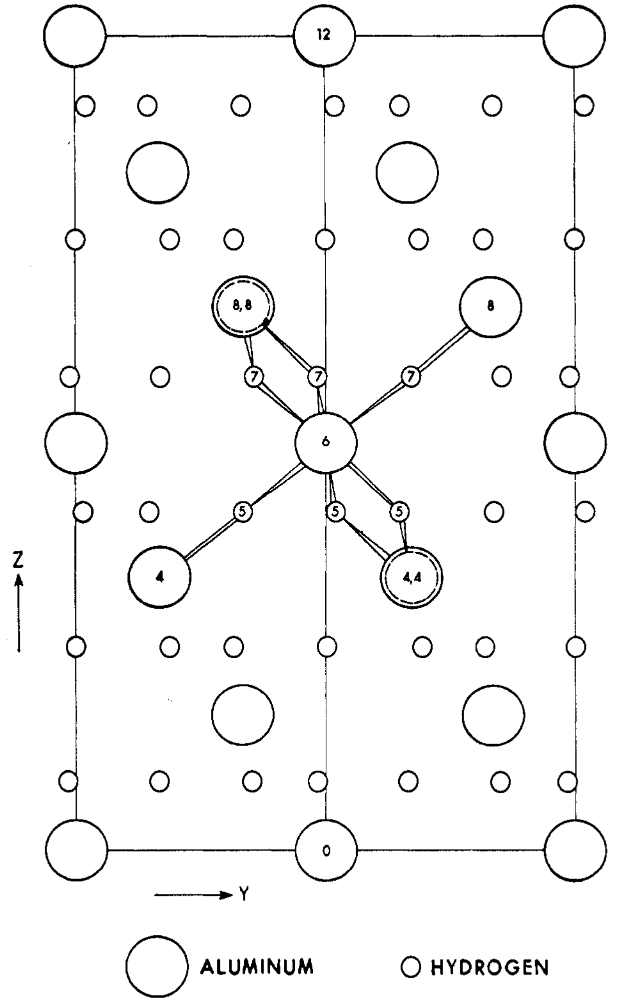

Figure 1.—Aluminum hydride structure as seen in the (100) projection of the hexagonal unit cell. The coordination of one aluminum atom is shown; numbers refer to twelfths of the unit cell dimension *c*.

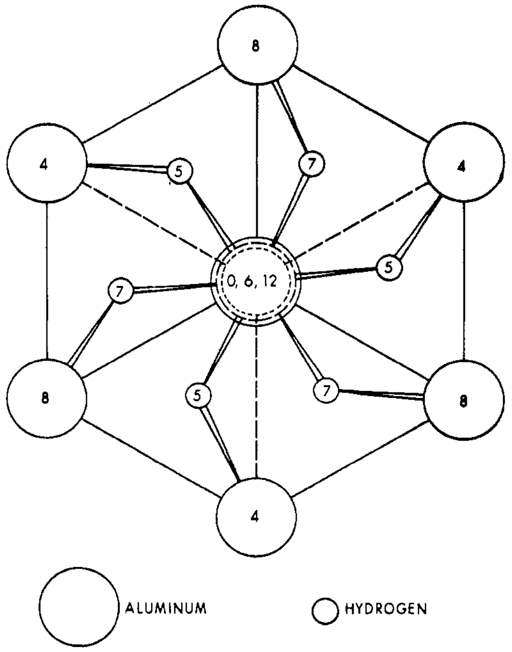

Figure 2.—The six Al···H···Al bridges formed by the aluminum atom at $^{1}/_{2}$, $^{1}/_{2}$, $^{1}/_{2}$ in the rhombohedral unit cell of aluminum hydride. Numbers refer to twelfths of dimension *c* of the hexagonal unit cell.

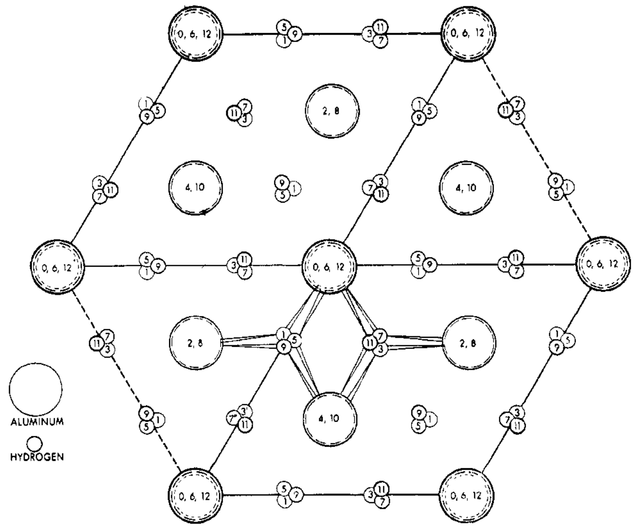

Figure 3.—Aluminum hydride structure as seen in the (001) projection of three hexagonal unit cells. Bridging involving the two kinds of hydrogen spirals is shown. Numbers refer to twelfths of the unit cell dimension *c*.

The octahedron of hydrogens surrounding the aluminum is slightly distorted as shown by the H···H distance of 2.434 Å between hydrogens in the coordination sphere in the planes above and below the aluminum and the distance 2.418 Å between hydrogens with one in the plane above and one in the plane below the aluminum. From this the radius of the hydrogen must be less than 2.42/2 = 1.21 Å. The Al···H···Al bond angle is 141.2°. The closest Al···Al approach is 3.236 Å between a bridged pair of atoms, and no metal–metal interaction occurs.

Figure 3 is a schematic drawing of the structure as viewed along the hexagonal *c* axis. The bridging of the three hydrogens on one spiral to the surrounding three columns of aluminum atoms is shown for both kinds of hydrogen spirals to illustrate the bridging network; three unit cells are shown to illustrate the packing. Aluminum atoms occur at intervals of $c/2$ along columns parallel to the *c* axis, with three columns per unit cell having atoms at $z = 0$ and 6 twelfths for one, $z = 2$ and 8 twelfths for another, and $z = 4$ and 10 twelfths for the third column. Hydrogens occur at intervals of $c/3$ along spirals which are also parallel to the *c* axis. There are six such spirals per unit cell—three with hydrogens at $z = 3$, 7, and 11 twelfths and three with hydrogens at $z = 1$, 5, and 9 twelfths. The columns and spirals are packed so that each column of aluminum atoms is hexagonally surrounded by six spirals of hydrogen atoms, three of each set of *z* coordinates, and each spiral of hydrogen atoms is surrounded hexagonally by three columns of aluminum atoms, one of each set of *z* coordinates, and three spirals of hydrogen atoms, all having the alternate set of *z* coordinates. Note that a given hydrogen atom on a spiral has six nearest neighbor hydrogen atoms, three in a plane $^{1}/_{12}c$ above and three in a plane $^{1}/_{12}c$ below.

Of these six, four are second neighbors in the bridging network and are at a distance of 2.418 Å, while the other two are bridged to aluminum atoms which are not in the three columns of aluminum atoms surrounding the spiral and are at a distance of 2.587 Å. To summarize, the bridging about one spiral of hydrogen atoms includes all six aluminum atoms in the surrounding three columns and one hydrogen atom, each at a different distance along z, in each of the surrounding three spirals. The result is a completely bridged structure which is a three-dimensional network of 3c–2e Al···H···Al bonds, consistent with the rather high observed crystalline density.

The structure is thermodynamically unstable with respect to decomposition to the elements.[25] Possibly, the layering of the hydride structure facilitates the release of H as H_2. The fact that the geometry of the Al atoms in the Al layer is the same as that in the metal,[26] except that the Al···Al distance in AlH_3 is 4.45 Å and in Al metal is 2.86 Å, suggests a mechanism of decomposition in which loss of H_2 is followed by a lattice contraction in the layer and a lattice expansion in the z axis direction, from 1.97 Å in the hydride to the 2.338 Å of Al metal.

Our AlH_3 structure appears to be isostructural with the essentially ionic structure of AlF_3[27] in which the $Al^{3+}\cdots F^-$ distance of 1.79 Å is slightly shorter than would be expected from the sum of ionic radii (1.86 Å). Three-center covalent bonding may be contributing to cause this shortening.

Acknowledgments.—We wish to thank Dr. L. K. Frevel for developing the intensity ratio calculation and providing liaison with Argonne National Laboratory and N. E. Matzek for suggesting the problem and supplying both the hydride and the deuteride. Least-squares and distance and angle calculations were performed using J. Gvildys' versions of Busing, Martin, and Levy's ORFLS and ORFFE programs on a CDC 3800 computer. Diffraction intensities were calculated using an ALGOL version of D. K. Smith's POWDER program on a Burroughs B5500 computer. This work was funded in part by Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, Calif., under Contract No. AF-04(611)-7554.

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The Crystal and Molecular Structure of Ytterbium Acetylacetonate Monohydrate(1)

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The crystal structure of $Yb(C_5H_7O_2)_3(H_2O)$, tris(acetylacetonato)aquoytterbium(III), has been determined from three-dimensional X-ray diffraction data collected by counter methods. A total of 2992 independent reflections, for which the intensity exceeded 1.07 times the background, were recorded as observed. Four molecules crystallize in a triclinic unit cell of symmetry $P\bar{1}$ and dimensions a = 13.01 Å, b = 18.33 Å, c = 8.32 Å, α = 100.40°, β = 102.12°, and γ = 105.19°. The calculated and observed densities are 1.72 and 1.74 g cm^{-3}, respectively. The structure has been refined by the method of least squares to a value of 0.076 for the conventional R factor. The two crystallographically independent ytterbium ions are seven-coordinate, each being bonded to three acetylacetonate groups and one water molecule. A hydrogen bond links the independent molecules in pairs. The coordination polyhedra formed about the independent ytterbium ions may both be described as capped trigonal prisms.

Introduction

The trisacetylacetonates of the lanthanides and ytterbium form metastable trihydrates which decompose to stable monohydrates.(4) A recent study(5) has shown that the dihydrated form is not an intermediate in the dehydration of the trihydrated chelate. However, the dihydrates of the lanthanum, praseodymium, neodymium, and samarium chelates can be prepared by recrystallizing the trihydrated form from cold 95% ethanol. We have previously determined the structure of yttrium acetylacetonate trihydrate(6) and lanthanum acetylacetonate dihydrate.(7)

The monohydrated forms of yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, dysprosium, holmium, erbium, and ytterbium have been prepared and character-

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