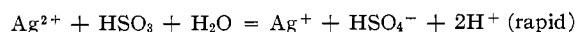
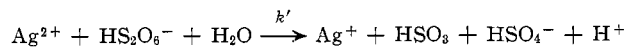
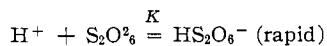


vided that subsequent rapid reactions are such as to satisfy the stoichiometry of the over-all reaction, which requires the formation of one sulfate for every Ag(II) consumed. Perhaps the simplest mechanism that is consistent with the results is



Then the observed rate constant k is given by $k = 2Kk'$. Another conceivable set of products in the rate-determining step could be $\text{Ag} + 2\text{HSO}_4^- + 3\text{H}^+$, provided a rapid completing reaction between Ag and Ag(II) follows. These two mechanistic possibilities differ in utilizing a one- or a two-electron change for silver, respectively. Other mechanisms arise as possibilities if one assumes that the predominant Ag(II)

species in solution is not the free aquo ion Ag^{2+} , but rather a complex such as $\text{Ag}(\text{S}_2\text{O}_6)_n^{2-2n}$. Under this assumption, the composition of the activated complex would be $\{\text{Ag}(\text{S}_2\text{O}_6)_{n+1}\text{H}^{1-2n}\}^\ddagger$. The present data do not establish clearly which of these mechanisms is correct, since dithionate was usually present in excess over silver(II).

Within the concentration range for which the most reliable data are available ($[\text{H}^+] = 2.0\text{--}3.0\text{ M}$, $[\text{Ag}^+] = 0.16\text{--}0.32\text{ M}$, $[\text{S}_2\text{O}_6^{2-}] = 0.025\text{--}0.050\text{ M}$, and $I = 3.4\text{--}3.5\text{ M}$), it appears that participation of silver(III) in the mechanism is not required. However, this does not preclude the possibility that under different conditions of concentrations or temperature, a path involving silver(III) might become important. In any case the data establish the participation of the oxidizing agent, silver(II), in the rate-determining step, in contrast to previously known reactions of dithionate with other oxidizing agents.

CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN, NEW YORK, AND THE BROOKHAVEN NATIONAL LABORATORY, UPTON, NEW YORK

The Crystal Structure of Lithium Aluminum Hydride

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The crystal structure of LiAlH_4 has been determined by single-crystal X-ray diffraction methods using counter detectors and filtered Cu $K\alpha$ radiation. The unit cell is monoclinic, $a = 4.845$, $b = 7.826$, and $c = 7.917$ Å (all ± 0.004 Å). The space group is $P2_1/c$ and there are four formula weights per unit cell. Each aluminum atom is surrounded at an average distance of 1.55 Å by four hydrogen atoms at the vertices of an almost regular tetrahedron. The lithium ions act as "bridges" between the tetrahydroaluminate ions; five hydrogen atoms surround the lithium ions, four at distances ranging from 1.88 to 2.00 Å and one at 2.16 Å.

Introduction

Large numbers of crystalline phases containing AlH_4^- and BH_4^- groups have been synthesized and studied in recent years; these compounds are widely used, particularly in preparative organic chemistry, and are of considerable theoretical interest. The literature contains many references to the tetrahedral configuration of the aluminohydride and borohydride groups in these phases,¹ but only one serious X-ray diffraction structure analysis of any of these materials appears to have been attempted prior to the present investigation: a powder diffraction study of alkali borohydrides.² In that work, which is sometimes cited as having established the tetrahedral configuration of both groups in the solid state, no effort was made to locate the hydrogen atoms directly from the experimental data. Our survey of the literature of this subject revealed no other experimental basis for that admittedly reasonable ex-

pectation. This work was therefore undertaken to investigate the configuration and the dimensions of the tetrahydroaluminate ion by a single-crystal X-ray diffraction study of lithium aluminum hydride.

Experimental Section

Lithium aluminum hydride crystallizes in the monoclinic system with $a = 4.845$, $b = 7.826$, and $c = 7.917$ Å (all ± 0.004 Å) and $\beta = 112.5 \pm 0.2^\circ$. The space group is $P2_1/c$ and there are four formula weights per unit cell: $d_{\text{calcd}} = 0.904$ g/cc and $d_{\text{measd}} = 0.92$ g/cc. The crystals grow in the form of rectangular parallelepipeds elongated along the c axis when solutions in diethyl ether are evaporated slowly. Because the crystals are highly hygroscopic, the specimens used for intensity measurements were sealed into thin-walled glass capillary tubes. Intensity data were collected with a scintillation counter and filtered copper $K\alpha$ radiation, using the θ - 2θ scan technique. The usual Lorentz and polarization corrections were applied to the data; absorption corrections were considered unnecessary since the maximum dimension of the crystal was 0.2 mm. The intensities of 507 reflections were measured and used in the structure analysis.

Structure Determination

Approximate positions of the aluminum atoms were obtained readily from the maxima on Patterson maps.

(1) (a) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p 119; (b) W. H. Stockmayer and C. C. Stephenson, *J. Chem. Phys.*, **21**, 1311 (1953); (c) P. T. Ford and R. E. Richards, *Discussions Faraday Soc.*, **19**, 239 (1955).

(2) A. M. Soldate, *J. Am. Chem. Soc.*, **69**, 987 (1947).

Two-dimensional electron density syntheses (*h*0*l*, 0*kl*, and *hk*0) yielded the positions of the lithium ions and verified the assumed positions of the aluminum atoms.

The crystal structure was refined by the least-squares method using the Brookhaven National Laboratory version of the Busing-Martin-Levy program.⁸ The refinement proceeded smoothly. The discrepancy coefficient, *R*, decreased rapidly to 10.4% when only aluminum and lithium ions were included in the calculations of structure factors. At this stage isotropic temperature factors were used. The positions of the hydrogen atoms were then obtained from a three-dimensional difference electron density map and the structure was further refined by least squares. All atoms were included in the calculations; anisotropic thermal parameters were assigned to aluminum and lithium, and isotropic thermal parameters to hydrogen. Initially all 507 observed reflections were assigned unit weights. After the calculations converged to stationary values, the weighting scheme was changed to

$$\sigma(F) = \left(\frac{1}{\sqrt{w}} \right) = 0.8 + 0.03F$$

and three additional least-squares cycles were computed.

Although the indicated parameter errors obtained with the latter scheme were consistently slightly smaller than those obtained when unit weights were used, the differences were never significant. In the final refinement cycle the changes in the position parameters of the aluminum and lithium atoms were all less than 1% of the coordinate errors indicated by the matrix inversion; changes in the hydrogen atom positions were less than 2% of the indicated errors. The final value of *R* was 3.2%

$$\left(R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \right)$$

Observed and calculated structure factors, based on the least-squares refinements, are listed in Table I; the final atomic and thermal parameters are given in Tables II and III. Interatomic distances and bond angles are listed in Tables IV and V.

Discussion

Anisotropic temperature factors of the aluminum and lithium ions and related data are listed in Table III. The aluminum thermal ellipsoid is almost spherical; the lithium ellipsoid is only slightly more anisotropic. The isotropic temperature factors of the four hydrogen atoms in the AlH_4^- group range from 1.76 to $2.04 \pm 0.56 \text{ \AA}^2$. The average is 1.93 \AA^2 , corresponding to an rms thermal radial displacement of 0.28 Å.

The hydrogen atoms are arranged about the aluminum at the vertices of a regular or almost regular tetrahedron. The average of the four aluminum-hydrogen distances is 1.547 Å, and the average of the six hydro-

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS ($\times 100$)

K	L	Obs	Cal	K	L	Obs	Cal	K	L	Obs	Cal	K	L	Obs	Cal
0	0	2206	2186	3	1	1868	1822	6	0	1968	1922	9	0	1868	1822
0	0	1868	1822	3	2	1968	1922	6	1	1868	1822	9	1	1868	1822
0	0	1468	1422	3	3	1568	1522	6	2	1468	1422	9	2	1468	1422
0	0	1068	1022	3	4	1168	1122	6	3	1068	1022	9	3	1068	1022
0	0	668	622	3	5	768	722	6	4	668	622	9	4	668	622
0	0	268	222	3	6	368	322	6	5	268	222	9	5	268	222
0	0	68	22	3	7	168	122	6	6	68	22	9	6	68	22
0	0	0	0	3	8	268	222	6	7	168	122	9	7	168	122
0	0	0	0	3	9	368	322	6	8	268	222	9	8	268	222
0	0	0	0	3	10	468	422	6	9	368	322	9	9	368	322
0	0	0	0	3	11	568	522	6	10	468	422	9	10	468	422
0	0	0	0	3	12	668	622	6	11	568	522	9	11	568	522
0	0	0	0	3	13	768	722	6	12	668	622	9	12	668	622
0	0	0	0	3	14	868	822	6	13	768	722	9	13	768	722
0	0	0	0	3	15	968	922	6	14	868	822	9	14	868	822
0	0	0	0	3	16	1068	1022	6	15	968	922	9	15	968	922
0	0	0	0	3	17	1168	1122	6	16	1068	1022	9	16	1068	1022
0	0	0	0	3	18	1268	1222	6	17	1168	1122	9	17	1168	1122
0	0	0	0	3	19	1368	1322	6	18	1268	1222	9	18	1268	1222
0	0	0	0	3	20	1468	1422	6	19	1368	1322	9	19	1368	1322
0	0	0	0	3	21	1568	1522	6	20	1468	1422	9	20	1468	1422
0	0	0	0	3	22	1668	1622	6	21	1568	1522	9	21	1568	1522
0	0	0	0	3	23	1768	1722	6	22	1668	1622	9	22	1668	1622
0	0	0	0	3	24	1868	1822	6	23	1768	1722	9	23	1768	1722
0	0	0	0	3	25	1968	1922	6	24	1868	1822	9	24	1868	1822
0	0	0	0	3	26	2068	2022	6	25	1968	1922	9	25	1968	1922
0	0	0	0	3	27	2168	2122	6	26	2068	2022	9	26	2068	2022
0	0	0	0	3	28	2268	2222	6	27	2168	2122	9	27	2168	2122
0	0	0	0	3	29	2368	2322	6	28	2268	2222	9	28	2268	2222
0	0	0	0	3	30	2468	2422	6	29	2368	2322	9	29	2368	2322
0	0	0	0	3	31	2568	2522	6	30	2468	2422	9	30	2468	2422
0	0	0	0	3	32	2668	2622	6	31	2568	2522	9	31	2568	2522
0	0	0	0	3	33	2768	2722	6	32	2668	2622	9	32	2668	2622
0	0	0	0	3	34	2868	2822	6	33	2768	2722	9	33	2768	2722
0	0	0	0	3	35	2968	2922	6	34	2868	2822	9	34	2868	2822
0	0	0	0	3	36	3068	3022	6	35	2968	2922	9	35	2968	2922
0	0	0	0	3	37	3168	3122	6	36	3068	3022	9	36	3068	3022
0	0	0	0	3	38	3268	3222	6	37	3168	3122	9	37	3168	3122
0	0	0	0	3	39	3368	3322	6	38	3268	3222	9	38	3268	3222
0	0	0	0	3	40	3468	3422	6	39	3368	3322	9	39	3368	3322
0	0	0	0	3	41	3568	3522	6	40	3468	3422	9	40	3468	3422
0	0	0	0	3	42	3668	3622	6	41	3568	3522	9	41	3568	3522
0	0	0	0	3	43	3768	3722	6	42	3668	3622	9	42	3668	3622
0	0	0	0	3	44	3868	3822	6	43	3768	3722	9	43	3768	3722
0	0	0	0	3	45	3968	3922	6	44	3868	3822	9	44	3868	3822
0	0	0	0	3	46	4068	4022	6	45	3968	3922	9	45	3968	3922
0	0	0	0	3	47	4168	4122	6	46	4068	4022	9	46	4068	4022
0	0	0	0	3	48	4268	4222	6	47	4168	4122	9	47	4168	4122
0	0	0	0	3	49	4368	4322	6	48	4268	4222	9	48	4268	4222
0	0	0	0	3	50	4468	4422	6	49	4368	4322	9	49	4368	4322
0	0	0	0	3	51	4568	4522	6	50	4468	4422	9	50	4468	4422
0	0	0	0	3	52	4668	4622	6	51	4568	4522	9	51	4568	4522
0	0	0	0	3	53	4768	4722	6	52	4668	4622	9	52	4668	4622
0	0	0	0	3	54	4868	4822	6	53	4768	4722	9	53	4768	4722
0	0	0	0	3	55	4968	4922	6	54	4868	4822	9	54	4868	4822
0	0	0	0	3	56	5068	5022	6	55	4968	4922	9	55	4968	4922
0	0	0	0	3	57	5168	5122	6	56	5068	5022	9	56	5068	5022
0	0	0	0	3	58	5268	5222	6	57	5168	5122	9	57	5168	5122
0	0	0	0	3	59	5368	5322	6	58	5268	5222	9	58	5268	5222
0	0	0	0	3	60	5468	5422	6	59	5368	5322	9	59	5368	5322
0	0	0	0	3	61	5568	5522	6	60	5468	5422	9	60	5468	5422
0	0	0	0	3	62	5668	5622	6	61	5568	5522	9	61	5568	5522
0	0	0	0	3	63	5768	5722	6	62	5668	5622	9	62	5668	5622
0	0	0	0	3	64	5868	5822	6	63	5768	5722	9	63	5768	5722
0	0	0	0	3	65	5968	5922	6	64	5868	5822	9	64	5868	5822
0	0	0	0	3	66	6068	6022	6	65	5968	5922	9	65	5968	5922
0	0	0	0	3	67	6168	6122	6	66	6068	6022	9	66	6068	6022
0	0	0	0	3	68	6268	6222	6	67	6168	6122	9	67	6168	6122
0	0	0	0	3	69	6368	6322	6	68	6268	6222	9	68	6268	6222
0	0	0	0	3	70	6468	6422	6	69	6368	6322	9	69	6368	6322
0	0	0	0	3	71	6568	6522	6	70	6468	6422	9	70	6468	6422
0	0	0	0	3	72	6668	6622	6	71	6568	6522	9	71	6568	6522
0	0	0	0	3	73	6768	6722	6	72	6668	6622	9	72	6668	6622
0	0	0	0	3	74	6868	6822	6	73	6768	6722	9	73	6768	6722
0	0	0	0	3	75	6968	6922	6	74	6868	6822	9	74	6868	6822
0	0	0	0	3	76	7068	7022	6	75	6968	6922	9	75	6968	6922
0	0	0	0	3	77	7168	7122	6	76	7068	7022	9	76	7068	7022
0	0	0	0	3	78	7268	7222	6	77	7168	7122	9	77	7168	7122
0	0	0	0	3	79	7368	7322	6	78	7268	7222	9	78	7268	7222
0	0	0	0	3	80	7468	7422	6	79	7368					

TABLE III
 ATOMIC THERMAL PARAMETERS^a

A. Anisotropic Thermal Factors						
	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Aluminum	0.0204 (4)	0.0073 (1)	0.0097 (1)	-0.0004 (1)	0.0057 (1)	-0.0003 (1)
Lithium	0.0387 (16)	0.0144 (6)	0.0139 (6)	0.0036 (8)	0.0098 (8)	-0.0027 (5)

B. Rms Displacements along Principal Axes of Thermal Ellipsoids, A			
	1	2	3
Aluminum	0.163 (1)	0.150 (1)	0.142 (1)
Lithium	0.226 (4)	0.191 (4)	0.180 (5)

C. Rms Radial Thermal Atomic Displacement, A	
Aluminum	0.263 (3)
Lithium	0.347 (7)
Hydrogen (av)	0.28 (7)

^a Estimated standard errors in parentheses.

TABLE IV

A. Intermetallic Distances (A) in LiAlH ₄ (Less than 5.0 A)		
Al-Al	Al-Li	Li-Al
3.753 ± 0.001	3.236 ± 0.004	3.186 ± 0.004
4.031 ± 0.002	3.265 ± 0.004	4.058 ± 0.004
4.512 ± 0.001	3.278 ± 0.004	4.084 ± 0.004
4.736 ± 0.002	3.297 ± 0.004	4.845 ± 0.004
4.845 ± 0.002	3.399 ± 0.004	4.905 ± 0.004
	3.734 ± 0.004	
	4.739 ± 0.004	

B. Shortest Li-H Distances (A) (Less Than 3.0 A)

1.883 ± 0.027	1.955 ± 0.028	2.158 ± 0.028
1.935 ± 0.027	1.997 ± 0.027	2.943 ± 0.028

configuration but neutron diffraction studies will probably be needed to settle that point.

The 12 shortest *intertetrahedral* hydrogen-hydrogen distances range from 2.67 to 2.99 A; these are significantly longer than the corresponding *intratetrahedral* distances whose average is 2.53 A (Table V).

The lithium ions are surrounded by four hydrogen atoms at distances ranging from 1.88 to 2.00 A; another hydrogen is at 2.16 A, and the next nearest is

TABLE V

DIMENSIONS OF THE TETRAHYDROALUMINATE ION

A. Bond Lengths, A

Al-H ₁	= 1.537 ± 0.026
Al-H ₂	= 1.516 ± 0.027
Al-H ₃	= 1.558 ± 0.025
Al-H ₄	= 1.578 ± 0.026
Al-H	= 1.547 A.

B. Bond Angles and Nonbonded Distances

A-Al-B	Angle, deg	Distance A-B, A
H ₁ -Al-H ₂	110.1 ± 1.4	2.502 ± 0.037 A.
H ₂ -Al-H ₃	109.5 ± 1.4	2.527 ± 0.037
H ₁ -Al-H ₄	113.7 ± 1.4	2.608 ± 0.038
H ₂ -Al-H ₃	109.8 ± 1.0	2.514 ± 0.036
H ₂ -Al-H ₄	104.8 ± 1.4	2.451 ± 0.037
H ₃ -Al-H ₄	108.9 ± 1.4	2.552 ± 0.037
Av	109.5	2.526

2.94 A from the lithium ion (Figure 1). The closest approaches are substantially smaller than the 2.04-A lithium-hydrogen distance in the highly ionic lithium hydride.⁴

(4) E. Zintl and A. Harder, *Z. Physik. Chem.*, **28B**, 478 (1935).