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

$$H^+ + S_2O_6^{2-} \overset{K}{=} HS_2O_6^- \text{ (rapid)}$$

$$Ag^{2+} + HS_2O_6^- + H_2O \xrightarrow{k'} Ag^+ + HSO_3 + HSO_4^- + H^+$$

$$Ag^{2+} + HSO_3 + H_2O = Ag^+ + HSO_4^- + 2H^+ \text{ (rapid)}$$

Then the observed rate constant k is given by $k = 2Kk'$. Another conceivable set of products in the rate-determining step could be $Ag + 2HSO_4^- + 3H^+$, 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 $Ag(S_2O_6)_n^{2-2n}$. Under this assumption, the composition of the activated complex would be $\{Ag(S_2O_6)_{n+1}H^{1-2n}\}^{\ddagger}$. 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 ($[H^+] = 2.0$–3.0 M, $[Ag^+] = 0.16$–0.32 M, $[S_2O_6^{2-}] = 0.025$–0.050 M, and $I = 3.4$–3.5 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

BY NATALIE SKLAR AND BEN POST

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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 Kα radiation. The unit cell is monoclinic, $a = 4.845$, $b = 7.826$, and $c = 7.917$ A (all ± 0.004 A). 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 A 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 A and one at 2.16 A.

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 expectation. 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.

(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).

Experimental Section

Lithium aluminum hydride crystallizes in the monoclinic system with $a = 4.845$, $b = 7.826$, and $c = 7.917$ A (all ± 0.004 A) and $\beta = 112.5 \pm 0.2°$. The space group is $P2_1/c$ and there are four formula weights per unit cell: $d_{calcd} = 0.904$ g/cc and $d_{measd} = 0.92$ 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 Kα 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.

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.[3] 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%

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

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 ± 0.56 A.[2] The average is 1.93 A,[2] corresponding to an rms thermal radial displacement of 0.28 A.

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 A, and the average of the six hydrogen–aluminum–hydrogen angles in the tetrahedron is 109.5° (Table V). The variation of individual hydrogen–aluminum–hydrogen angles and of the intratetrahedral hydrogen–hydrogen distances indicates a possible slight distortion of the tetrahedron from the ideal

(3) W. R. Busing, K. Martin, and H. A. Levy, ORNL-TM-305, Oak Ridge National Laboratory, 1962.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS (×100)

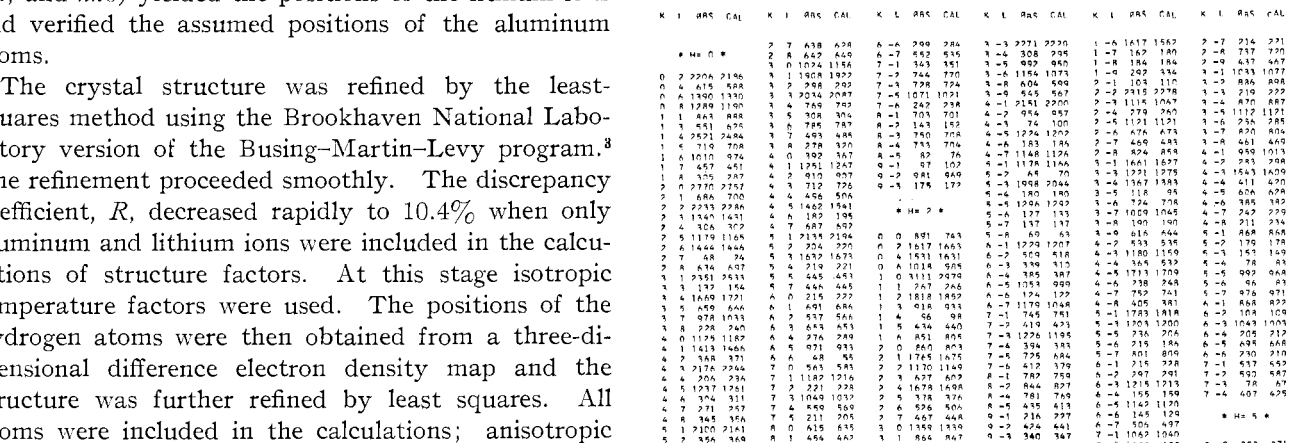

TABLE II

ATOMIC COORDINATES[a] IN $LiAlH_4$

	x	*y*	*z*
Aluminum	0.14033 (10)	0.20131 (6)	0.93151 (6)
Lithium	0.56896 (82)	0.46604 (44)	0.82164 (46)
Hydrogen (1)	0.2005 (63)	0.1020 (33)	0.7816 (36)
Hydrogen (2)	0.3120 (60)	0.3682 (34)	0.9709 (34)
Hydrogen (3)	0.2382 (60)	0.0911 (31)	0.1087 (33)
Hydrogen (4)	0.8032 (59)	0.2552 (36)	0.8760 (35)

[a] Estimated standard errors in parentheses.

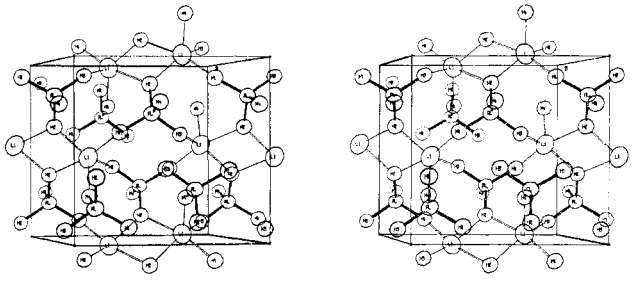

Figure 1.—Stereo pair view (*ca.* along *a*) of unit cell of $LiAlH_4$; *b* axis vertical and *c* axis horizontal.

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 *inter*tetrahedral hydrogen–hydrogen distances range from 2.67 to 2.99 A; these are significantly longer than the corresponding *intra*tetrahedral 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 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]

TABLE V

DIMENSIONS OF THE TETRAHYDROALUMINATE ION

A. Bond Lengths, A

$Al–H_1 = 1.537 \pm 0.026$
$Al–H_2 = 1.516 \pm 0.027$
$Al–H_3 = 1.558 \pm 0.025$
$Al–H_4 = 1.578 \pm 0.026$
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_5	108.9 ± 1.4	2.552 ± 0.037
Av	109.5	2.526

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