S_4N_3Cl obtained from the synthetic procedure described above may therefore be attributable to the oxidation of a significant proportion of NH_4Cl to elementary nitrogen.

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CONTRIBUTION FROM REACTOR CHEMISTRY AND CHEMISTRY
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Crystal Structures of Rubidium Lithium Fluoride, $RbLiF_2$, and Cesium Lithium Fluoride, $CsLiF_2$[1]

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The existence of $RbLiF_2$ and $CsLiF_2$ was established during thermal analysis studies of molten salt systems by Barton, *et al.*,[2] who showed these to be the only intermediate compounds in the binary systems RbF–LiF and CsF–LiF. The crystal structures of the compounds are of interest because each consists of ions of well-known radii which are expected to pack together in such a manner as to obtain the maximum number of cation–anion contacts consistent with their radius ratios. However, in the component alkali fluorides, for reasons not yet known,[3] the Rb^+ and Cs^+ ions, which are capable of larger coordination numbers, and the Li^+ ion, whose radius is near the lower limit for octahedral coordination, all have the sixfold coordination of the NaCl structure. Thus the present X-ray study was undertaken to determine the type of coordination adopted by the same ions in these difluorides.

Experimental

The compounds $RbLiF_2$ and $CsLiF_2$ melt incongruently at 475 and 495°, respectively, and precipitate as the primary phase from melts within a small range of compositions near 55 mole % RbF (or CsF) and 45 mole % LiF. By slowly cooling melts in this composition range crystals for X-ray study were obtained, along with some of the eutectic mixtures which the difluorides form with RbF or CsF. The resulting material was very hygroscopic, and the separation of crystals from the eutectic mixture was performed by submersion of the products in oil and examination under a microscope. A marked tendency of the material to twin on {001} when subjected to a shearing force added to the difficulty of obtaining single crystals. A single crystal of $RbLiF_2$ was obtained, but for $CsLiF_2$ a specimen, about 10% of which was oriented in a twin relationship to the main crystal, was used. The samples selected were sealed in glass capillaries before removal from the oil.

X-Ray precession photographs taken with Mo radiation yielded the following monoclinic crystal data. $RbLiF_2$: $a = 5.83 \pm 0.01$, $b = 11.16 \pm 0.02$, $c = 7.86 \pm 0.02$ Å., $\beta = 94° 55' \pm 5'$; $CsLiF_2$: $a = 6.01 \pm 0.02$, $b = 11.64 \pm 0.02$, $c = 8.18 \pm 0.02$ Å., $\beta = 90° 45' \pm 5'$. The presence of hkl only for $h + k = 2n$ and $h0l$ only for $l = 2n$ indicated the probable space group C2/c or Cc. There are eight formula weights per unit cell.

On the basis of these data a trial structure for $CsLiF_2$ was obtained by means of a computer program[4] which postulated possible atomic arrangements and evaluated them by comparing calculated and observed structure factors for 13 reflections. Structures were generated by advancing the atoms across a grid of points in the basic asymmetric unit until all acceptable combinations of positions had been obtained. The number of positions scanned was greatly reduced by rejecting those for which some interatomic distances were shorter than the sum of the corresponding ionic radii. Because precession photographs showed that the symmetry of $CsLiF_2$ was very nearly that of the orthorhombic space group Cmca, the number of trial structures to be tested was further reduced by assuming this approximate symmetry.

An estimate of the Coulomb energy was also calculated for each postulated arrangement, and this proved especially useful as a criterion for placing the Li atom, which makes only a small contribution to the structure factor. The best trial structure was nearly that described by the final parameters (space group C2/c) in Table I. Later $RbLiF_2$ was shown to be isostructural with $CsLiF_2$.

TABLE I

PARAMETERS AND STANDARD DEVIATIONS FROM LEAST-SQUARES REFINEMENT

Site	Atom	x (σ)[a]	y (σ)[a]	z (σ)[a]	B (σ)[a]
			$RbLiF_2$		
8(f)	Rb	0.2649 (5)	0.4105 (3)	0.0713 (5)	1.73 (6)
8(f)	Li	0.215 (9)	0.191 (6)	0.351 (8)	2.5
8(f)	F(1)	0.219 (3)	0.362 (2)	0.416 (3)	1.4 (3)
4(e)	F(2)	0	0.116 (2)	$^1/_4$	1.8 (5)
4(c)	F(3)	0	0.682 (2)	$^1/_4$	2.1 (5)
			$CsLiF_2$		
8(f)	Cs	0.2528 (3)	0.4089 (2)	0.0725 (2)	1.96 (5)
8(f)	Li	0.25 (1)	0.209 (4)	0.362 (7)	2.5
8(f)	F(1)	0.244 (3)	0.357 (2)	0.423 (2)	2.2 (3)
4(e)	F(2)	0	0.151 (2)	$^1/_4$	2.4 (4)
4(e)	F(3)	0	0.663 (3)	$^1/_4$	3.0 (5)

[a] The σ applies to the last significant figure for each entry.

The proposed structure was verified by measurement of a sampling of the three-dimensional X-ray reflections. For this purpose a single-crystal orienter was used with the 2θ-scan technique. Mo Kα X-rays were detected by a scintillation counter. The inherent accuracy of the equipment was not attained, however, due to the properties of the crystal specimens, namely, irregular shape plus high absorption, presence of oil and glass, and, for $CsLiF_2$, at least, the presence of partial twinning. Some 137 reflections for $RbLiF_2$ and 149 reflections for $CsLiF_2$ were measured, corrected for Lorentz-polarization effects and a spherical absorption factor ($\mu R = 1.46$ for $RbLiF_2$; $\mu R = 1.07$ for $CsLiF_2$), and reduced to structure factors.

The parameters of the trial structure were refined by iterative least squares[5] to the final values in Table I. An isotropic temperature factor was varied for each atom except lithium, for which a constant value was assigned. Atomic form factors and the real and imaginary dispersion corrections were taken from

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

[2] C. J. Barton, T. N. McVay, L. M. Bratcher, and W. R. Grimes, "Phase Diagrams of Nuclear Reactor Materials," R. E. Thoma, Ed., Oak Ridge National Laboratory Report ORNL-2548, Nov. 2, 1959.

[3] A. F. Wells, "Structural Inorganic Chemistry," 3rd Ed., Oxford University Press, London, 1962, p. 76.

[4] W. R. Busing, Abstracts, Villanova Meeting of the American Crystallographic Association, 1962, p. 20; Oak Ridge National Laboratory Report ORNL-3320, June 20, 1962, p. 115.

[5] W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least-Squares Program," Oak Ridge National Laboratory Report ORNL-TM-305, 1962.

the International Tables.[6] The refinement was based on F^2; a weighting scheme, based on estimated variances and described elsewhere,[7] was used. Observed and calculated structure factors are listed in Table II. The residual

$$R = \Sigma\left||F_o| - |F_c|\right|/\Sigma|F_o|$$

was 0.079 for $RbLiF_2$ and 0.069 for $CsLiF_2$.

TABLE II

OBSERVED (FO) AND CALCULATED (FC) STRUCTURE FACTORS ON AN ABSOLUTE SCALE. VALUES FOR $RbLiF_2$ ARE ABOVE, FOR $CsLiF_2$ BELOW

H	L	FO	FC
* K = 0 *			
2	0	470	463
4	0	402	387
6	0	151	143
8	0	94	87
10	0	0	20
2	-2	523	510
4	-2	268	260
6	-2	239	234
8	-2	98	107
10	-2	55	65
0	2	240	235
2	2	273	281
4	2	0	11
6	2	43	18
8	2	26	34
2	-4	123	112
4	-4	91	79
6	-4	41	43
8	-4	65	70
0	4	65	61
2	4	243	253
4	4	135	131
6	4	137	140
8	4	65	66
2	-6	203	198
4	-6	190	187
6	-6	52	64
8	-6	0	39
0	6	321	330
2	6	220	217
4	6	202	210
6	6	81	100
8	6	53	66
2	-8	226	217
4	-8	148	143
6	-8	122	125
8	-8	48	59
0	8	160	154
2	8	165	159
4	8	64	65
6	8	31	45
2	-10	49	34
4	-10	87	74
6	-10	60	49
0	10	47	37
2	10	27	20
4	10	30	13
2	-12	41	37
0	12	79	69
* K = 1 *			
1	0	50	49
3	0	60	46
5	0	84	77
7	0	54	56
3	1	123	123
3	-5	43	31
* K = 2 *			
2	0	191	178
4	0	94	87
6	0	57	69
0	1	141	132
0	2	158	156
2	2	67	63
0	3	493	549
2	3	316	321
4	4	41	55
0	5	208	207
0	6	88	89
0	7	0	9
0	8	83	78
0	9	144	150
0	11	60	80
* K = 3 *			
1	0	40	32
3	0	28	2
1	-3	160	152
5	-3	131	134
* K = 4 *			
2	0	270	262
4	0	219	214
6	0	77	85
0	1	203	191
0	2	156	152
0	3	229	227
4	3	162	147
0	5	169	167
0	6	193	202
0	8	94	96
0	9	58	67
* K = 5 *			
1	0	110	100
5	0	82	94
* K = 6 *			
2	0	303	280
4	0	197	184
6	0	122	122
0	1	62	68
0	2	195	207
0	3	138	144
2	3	86	93
0	5	60	44
0	6	157	166
0	8	131	134
* K = 7 *			
1	0	19	18
3	0	83	90
5	0	72	75
1	2	233	247
1	4	171	180
3	5	111	116
* K = 8 *			
4	0	40	25
0	1	88	95
0	2	15	11
0	3	194	215
4	4	20	3
0	5	143	146
0	6	0	6
* K = 9 *			
1	0	42	40
1	-2	78	86
3	2	82	81
1	5	139	159
* K = 10 *			
2	0	138	128
4	0	114	117
6	0	63	60
0	1	55	41
0	2	96	74
0	3	90	95
0	5	73	75
* K = 11 *			
3	0	75	75
3	2	143	156
* K = 12 *			
2	0	127	130
4	0	68	91
6	0	71	62
0	1	0	6
0	2	90	90
0	3	54	61
0	5	48	29
0	6	100	79
* K = 14 *			
2	0	0	24
0	1	76	62
0	2	0	20
0	3	104	99
0	5	72	77
* K = 16 *			
0	2	69	57

H	L	FO	FC
* K = 0 *			
2	0	641	733
4	0	587	601
6	0	289	298
8	0	197	187
10	0	91	84
2	-2	534	574
4	-2	261	280
0	2	423	407
2	2	571	522
4	2	229	217
8	2	67	70
4	-4	50	51
0	4	118	115
4	4	120	112
0	6	485	480
0	8	264	248
0	10	49	45
0	12	104	98
0	14	82	75
* K = 1 *			
5	0	26	25
3	-3	88	73
3	3	88	55
5	3	36	29
3	5	123	113
1	-6	140	136
3	6	100	96
1	-7	192	170
7	8	54	49
* K = 2 *			
4	0	144	141
4	-1	109	119
0	1	247	240
4	1	170	183
4	-2	125	132
4	-3	401	433
0	3	704	766
4	3	450	438
0	-4	71	64
4	-4	38	29
0	4	71	64
2	4	28	12
2	-5	431	402
0	6	145	135
2	7	54	57
0	8	116	115
0	9	219	214
0	11	137	133
0	13	35	34
* K = 3 *			
3	-2	25	23
3	2	27	21
3	-3	95	95
5	3	24	27
3	-4	13	16
1	-5	304	281
1	5	317	278
* K = 4 *			
2	0	385	403
4	0	341	343
8	0	118	112
4	1	183	184
4	2	147	136
0	3	347	341
2	3	429	402
4	3	250	238
0	-4	46	52
4	4	52	59
0	5	257	263
2	-6	230	219
0	7	40	29
0	8	168	160
0	9	108	112
0	10	27	23
0	11	102	106
0	12	60	63
* K = 5 *			
3	-1	154	164
3	1	159	160
5	1	89	92
3	-2	273	293
3	2	348	336
1	-3	33	41
1	-4	452	421
1	4	480	435
3	4	362	335
3	5	99	86
1	-6	171	154
1	-7	118	114
1	7	118	107
* K = 6 *			
2	0	437	498
2	-1	100	114
2	1	132	129
2	-2	208	216
4	-2	217	238
2	2	224	195
4	2	206	205
0	-3	219	218
4	-3	123	132
0	3	223	218
2	4	69	58
2	-5	123	102
2	5	114	93
6	-6	135	135
0	8	199	208
0	9	51	58
6	9	12	26
0	10	21	16
0	11	46	39
0	12	64	58
* K = 7 *			
3	0	18	26
3	1	268	258
1	-2	307	289
3	2	259	242
1	-3	82	79
3	-3	61	60
3	3	48	45
1	-4	301	293
1	-5	177	177
1	-6	68	75
1	6	65	78
* K = 8 *			
2	0	35	30
0	-1	210	214
2	-1	93	100
4	-1	111	124
0	1	208	214
2	-4	31	8
2	-5	198	200
2	5	200	187
0	9	115	121
0	11	105	106
* K = 9 *			
1	-2	137	147
3	2	114	125
1	-3	76	71
1	-4	142	135
1	4	154	140
* K = 10 *			
0	-1	66	66
2	-2	123	128
2	2	120	116
0	8	119	124
0	9	64	58
0	10	29	12
2	10	31	19
0	11	36	44
* K = 11 *			
5	-4	157	170
5	6	42	43
* K = 12 *			
2	0	162	184
0	8	87	94
0	9	30	40
* K = 13 *			
3	-5	122	96
* K = 14 *			
0	1	79	78
0	9	73	74
* K = 16 *			
0	9	29	19

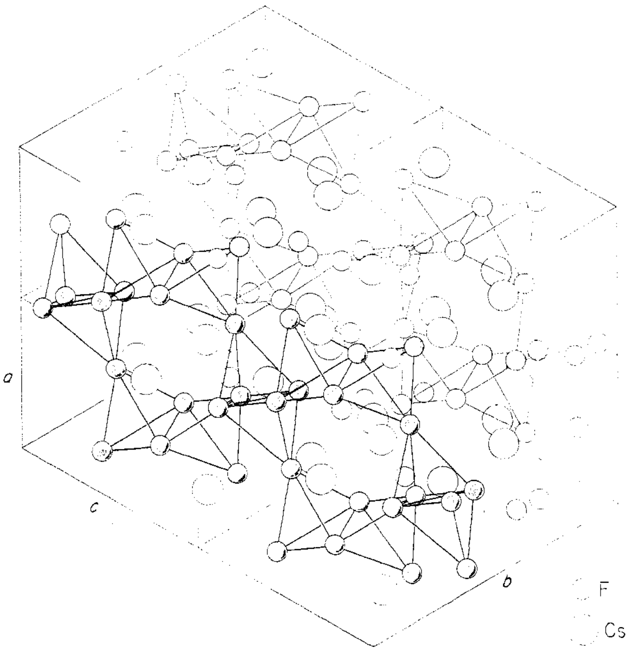

Figure 1.—Schematic drawing of the structure of $CsLiF_2$. Each tetrahedron of fluoride ions encloses a lithium ion, but it is omitted from the drawing for clarity.

Results and Discussion

A schematic drawing of the structure of $CsLiF_2$ is given in Figure 1; isostructural $RbLiF_2$ is visualized by replacing Cs^+ ions with Rb^+ ions. One Li^+ ion is situated within each tetrahedron of F^- ions but is omitted from the illustration for clarity. Each tetrahedron shares one edge and two corners with other tetrahedra forming a sheet parallel to (001), such as the one shaded in Figure 1. Between the sheets and binding them together are found the Cs^+ (Rb^+) ions.

Interionic distances were calculated[8] up to 4 Å.; those within each coordination group are listed in Table III. Since some systematic error is present in the data (see Experimental section), the limits of error in the distances should be taken larger than those implied by the σ values, which were obtained from least-squares refinement. Thus, it is doubtful that the indicated wide variation in Li–F distances is real. In fact, Hamilton's[9] R-factor ratio test shows that the models indicated by Table I are not better at the 90% confidence level than ones in which the Li atoms are equidistant from the surrounding F atoms (at distances of 1.86 Å. in $CsLiF_2$ and 1.87 Å. in $RbLiF_2$). The irregular shape of the tetrahedra is probably significant,

TABLE III

CORRESPONDING INTERIONIC DISTANCES IN $RbLiF_2$ AND $CsLiF_2$, IN Å.

$RbLiF_2$			$CsLiF_2$		
Li–F,[a] σ	F···F,[a] σ	Rb–F, σ	Li–F,[a] σ	F···F,[a] σ	Cs–F, σ
1.97 ± 0.06	2.83 ± 0.04[b]	2.78 ± 0.02	1.80 ± 0.05	2.79 ± 0.04[b]	2.94 ± 0.02
1.90 ± 0.06	2.99 ± 0.01	2.82 ± 0.02	1.86 ± 0.06	3.04 ± 0.02	2.99 ± 0.02
1.64 ± 0.06	2.96 ± 0.02	2.87 ± 0.02	1.89 ± 0.06	3.08 ± 0.02	3.08 ± 0.02
1.92 ± 0.06	2.96 ± 0.03	3.04 ± 0.02	1.92 ± 0.06	3.09 ± 0.03	3.12 ± 0.02
	3.04 ± 0.02	2.97 ± 0.01		3.10 ± 0.02	3.14 ± 0.01
	3.24 ± 0.03	3.01 ± 0.01		3.14 ± 0.03	3.15 ± 0.01
		2.96 ± 0.02			3.50 ± 0.02
		3.16 ± 0.02			3.53 ± 0.02

[a] Within the LiF_4 tetrahedron. [b] Shared edge.

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(6) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962.

(7) J. H. Burns, *Inorg. Chem.*, **4**, 881 (1965).

(8) W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Function and Error Program" Oak Ridge National Laboratory Report ORNL-TM-306, 1964.

(9) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

however, since the observed shortening of the edges shared by tetrahedra is in accord with Pauling's rules for stability of ionic crystals.[10]

Around each Rb^+ ion are eight F^- ions at distances ranging from 2.78 to 3.16 Å. (average 2.95 Å.) in an asymmetrical array. The array approximates very roughly an antiprism with its $\bar{4}$ axis along *b*. A similar grouping occurs around the Cs^+ ion, but six F^- ions are at distances of 2.96 to 3.15 Å. (average 3.07 Å.) and two are at 3.50 and 3.53 Å. Since the interatomic distances from Pauling's crystal radii are r(Rb–F) = 2.95 Å. (eight-coordination) and r(Cs–F) = 3.05 Å. (six-coordination), it is appropriate to designate the coordination numbers of Rb^+ and Cs^+ ions in the two compounds as eight and six, respectively. Thus it appears that, while the sheets of tetrahedra make available about the same configuration of anions to each kind of large cation, the Rb^+ ion attracts more neighbors than the Cs^+ ion, which is to be expected considering their relative anion : cation radius ratios.[3]

Acknowledgment.—We thank G. M. Hebert for preparing the samples and R. E. Thoma for suggesting this problem.

[10] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 561.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PURDUE UNIVERSITY, LAFAYETTE, INDIANA

Isotope Effects in Boron Hydrides. X.[1] The Reaction of Diborane with Basic D_2O

BY ROBERT EARL DAVIS[2a] AND JUDITH ANN GOTTBRATH[2b]

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In earlier papers of this series the kinetic isotope effects of numerous hydride transfer reactions have been reported. In continuing these studies of complex isotope effects, it seemed important to vary the number of deuterium atoms on borohydride ion and also study the reaction of borane (or diborane) with heavy water. In this way one could obtain further insight into the primary inverse isotope effect of 0.70 in the acid hydrolysis of sodium borohydride.[3] Since aquated borane was suggested as a reaction intermediate we surveyed

$$BH_4^- + 4H_2O \longrightarrow 4H_2\uparrow + B(OH)_4^- \qquad (1)$$

$$BD_4^- + 4H_2O \longrightarrow 4HD\uparrow + B(OH)_4^- \qquad (2)$$

the literature for the reaction of diborane and other boranes with aqueous base[4] and then experimentally rediscovered the synthesis of sodium borohydride.[5,6]

Since early data[7] suggested rather unusual isotopic rearrangements, and since it was wished to prepare and study the mixed isotopic species, $NaBH_{4-x}D_x$, gaseous diborane, B_2H_6, in a stream of nitrogen was allowed to react with an aqueous solution of sodium hydroxide and also with sodium deuteroxide, NaOD, in heavy water at 4°.

Diborane was generated by the gradual addition of solid sodium borohydride to methanesulfonic acid.[8] Pure nitrogen swept the diborane through a safety trap, a cold trap at −78°, and then a fritted gas dispersion tube placed under a solution of aqueous sodium hydroxide (0.10 or 1.0 *M*). A sample of the solution was then treated with dilute acid to decompose any boron hydride and the total amount of boron obtained. Another sample was treated with excess iodate and the amount of the hydride determined. In different experiments, it was determined that 83 to 90% of the diborane reacted immediately to produce borate and hydrogen.

$$B_2H_6 + 2OH^- + 6H_2O \longrightarrow 2B(OH)_4^- + 6H_2 \qquad (3)$$

However, 10 to 17% of the diborane produced sodium borohydride.

$$B_2H_6 + 2OH^- + 2H_2O \longrightarrow B(OH)_4^- + BH_4^- + 2H_2 \qquad (4)$$

The current experiments did not seek to maximize the yield of borohydride, but somewhat greater yields were realized if the addition of diborane was slow and the ratio of nitrogen to diborane large.

Diborane was passed into solutions of 0.1 *M* sodium deuterioxide at 4° in heavy water of 99.62% isotopic purity. The excess water was then removed under very high vacuum at 0°. The powdery residues containing sodium borate and sodium deuterioxide were added to borate buffers in *a large excess* of light water. The evolved gases were analyzed for deuterium (as HD) using a mass spectrometer. The results are presented in Table I. Essentially all of the hydridic hydrogens arise from the diborane. It is unlikely that exchange between hydrogen gas (produced by hydrolysis) and diborane contributes significantly to the present reaction.[9,10] Since the total amount of sodium deuterioxide added is known and since the isotopic purity of the heavy water is known, the total amount of any deu-

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[1] Paper VIII: R. E. Davis, C. L. Kibby, and C. G. Swain, *J. Am. Chem. Soc.*, in press; paper IX: *Chem. Commun.* (London), in press.

[2] (a) Alfred P. Sloan Fellow, 1962–1966; (b) N.S.F. Summer Research Participant, 1961.

[3] Paper III: R. E. Davis, E. Bromles, and C. L. Kibby, *J. Am. Chem. Soc.*, **84**, 885 (1962). The hydrolysis of borohydride in aqueous solution containing trimethylamine produced trimethylamine borane. Recently Collat [J. A. Gardiner and J. W. Collat, *J. Am. Chem. Soc.*, **87**, 1692 (1965)] has obtained evidence for a species as BH_3OH^-, a species first postulated by J. Goubeau and H. Kallfass [*Z. anorg. allgem. Chem.*, **299**, 160 (1959)].

[4] R. C. Ray, *J. Chem. Soc.*, **121**, 1088 (1922); R. C. Ray, *Chem. Ind.* (London), 322 (1946); M. W. Travers and R. C. Ray, *Proc. Roy. Soc.* (London), **A87**, 163 (1912); A. Stock and E. Kuss, *Ber.*, **47**, 810 (1914); A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933; A. Stock, W. Sutterlin, and Z. Kurzen, *Z. anorg. allgem Chem.*, **225**, 225 (1935); L. Klemm and W. Klemm, *ibid.*, **225**, 258 (1935).

[5] R. E. Davis and J. A. Gottbrath, *Chem. Ind.* (London), 1961 (1961).

[6] P. F. Winternitz, U. S. Patent 2,532,217 (Nov. 28, 1950); *Chem. Abstr.*, **45**, P2162 (1951). Unfortunately *Chemical Abstracts* has abstracted this patent *only* as to the reaction of LiH with BF_3 and *no* mention is made in this abstract of the reaction of diborane with aqueous potassium hydroxide. Had we known this, we would not have published our earlier paper[5] on "The Nature of Stock's Hypoborate." The "Official Gazette" of the U. S. Patent Office contains *only* the abstract on the lithium hydride reaction [**640**, (4) 1354 (1950)].

[7] W. L. Jolly and R. E. Mesmer, *J. Am. Chem. Soc.*, **83**, 4470 (1961).

[8] H. G. Weiss and I. Shapiro, *ibid.*, **81**, 6167 (1959).

[9] R. A. Marcus, *J. Chem. Phys.*, **23**, 1107 (1955).

[10] P. C. Maybury and W. S. Koski, *ibid.*, **21**, 742 (1953).