sented (eq. 3). The two-term denominator, $\kappa + [I^-]$, suggests the operation of a two-step-mechanism, either step of which may become rate-determining, depending upon the relative magnitudes of κ and $[I^-]$; it also suggests that solvent and iodide ion compete for an intermediate present at its steady-state concentration. The rate law reveals the compositions of the activated complex in each step; these are (CrI_3^{2+}) and (CrI_2^{3+}), respectively.

A mechanism consistent with the observed kinetics of the reaction is given by the following reaction sequence (in which coordinated solvent molecules have been omitted)

$$CrI^{2+} + I_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} CrI_2^{3+} + I^- \qquad (k_1 \ll k_2) \tag{6}$$

$$CrI_2^{3+} \xrightarrow{k_3} Cr^{3+} + I_2 \tag{7}$$

$$I_2 + I^- \rightleftarrows I_3^- \qquad (\text{rapid; } Q = 787\ M^{-1})$$

The spontaneous aquation was also included and the steady-state procedure applied to the postulated unstable intermediate in this reaction, resulting in the equation

$$-\mathrm{d} \ln [CrI^{2+}]/\mathrm{d}t = k_{aq} + (k_1k_3/k_2)[I_2]/(k_3/k_2 + [I^-])$$

which is of the same form as the experimental rate law (eq. 3), with the empirical constants k and κ identified as k_1k_3/k_2 and k_3/k_2, respectively.

It is useful to compare these results with those obtained in the study of the CrI^{2+}–IO_3^- reaction (eq. 5), the rate law for which resembles that found in the present work under comparable circumstances, namely the limiting form with $[I^-] = 0$.[8] Although it is tempting to interpret the identical form of the two rate laws as indicating a similarity of mechanism, this leads to quantitative difficulties. The present study has $k/\kappa = 2.9 \pm 0.1\ M^{-1}$ sec.$^{-1}$ at 25.0° and 1.00 F $HClO_4$, whereas $k_{ox} = 10.7\ M^{-1}$ sec.$^{-1}$ under the same conditions. It appears, therefore, that although the oxidation reaction proceeds necessarily in part by a path in which iodine catalyzes the decomposition of CrI^{2+}, this path cannot quantitatively account for the entire course of reaction.[9]

The reactions of CrI^{2+} with I_2 and IO_3^- constitute an example of a pair of reactions for which the activated complexes in the rate-determining steps at low $[I^-]$ have the same composition, but are, in fact, not the same (presumably the geometry of the three iodine atoms is different in the two activated complexes). Another interesting feature of the CrI^{2+}–I_2 reaction is the failure of the bimolecular path, forming directly Cr^{3+} and I_3^-, to compete with the two-step sequence required by the rate equation.

The second step of the reaction represents aquation of an iodine–chromium(III) complex; these data allow only a lower limit to be set on its specific aquation rate, namely $k_3 = \kappa k_2 \gg 5.1 \times 10^{-5}$ sec.$^{-1}$ at 25.0°.

Acknowledgment.—The author is grateful to Prof. E. L. King for helpful comments concerning the kinetic data and some implications of the proposed reaction mechanism.

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[8] The circumstances are comparable for the reason that iodide ion cannot accumulate in the presence of IO_3^-—it is rapidly and completely oxidized to iodine.

[9] It is worth commenting on a semiquantitative experiment on the CrI^{2+}–I_2 reaction described in the earlier study (ref. 2) on the CrI^{2+}–IO_3 reaction. This experiment involved ~0.005 M CrI^{2+} and ~0.001 F I_2 in 1 F $HClO_4$; it was observed that the iodine-catalyzed aquation occurred at a negligible rate relative to that of the CrI^{2+}–IO_3 reaction. The apparent failure of iodine as a catalyst here is due to its concentration relative to that of CrI^{2+}: the so-called catalyst is largely converted to the inactive form I_3^- after only ~20% reaction.

Contribution from the Department of Chemistry,
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Complex Metal Oxides of the Type $AMMo^{IV}{}_3O_8$

By Josephine DeBenedittis and Lewis Katz

Received August 23, 1965

The preparation and structure of compounds of the type $A^{II}{}_2Mo^{IV}{}_3O_8$, where A^{II} may be Mg, Mn, Fe, Co, Ni, Zn, or Cd, have been reported.[1] More recently, an apparently related lithium–scandium–molybdenum(IV) oxide has been reported.[2]

The $A_2Mo_3O_8$ compounds were shown to have a hexagonal unit cell with four close-packed layers of oxygens. One of the divalent ions is in a tetrahedral hole, and the other is in an octahedral hole. The molybdenum ions are in octahedral holes and the octahedra share edges in such a way as to form rings of three molybdenums. Both the closeness of approach of the molybdenum atoms in the rings and the very low magnetic susceptibility of the compounds indicate Mo–Mo bonding.

From the starting reactant composition, the formula postulated for the lithium–scandium–molybdenum oxide was $LiScMo_3O_8$, and the structure was assumed to be related to that of $A_2Mo_3O_8$, with the monovalent lithium and the trivalent scandium substituted for the two divalent A cations. The c axis of the new compound is only half as long as that of the $A_2Mo_3O_8$ compounds, so the structure was assumed to repeat after two layers of oxygens rather than four.

In this note we present chemical evidence for the formula $LiScMo_3O_8$, evidence for the existence of additional compounds of the same type, in particular $LiYMo_3O_8$ and $LiGaMo_3O_8$, and X-ray powder data in support of the postulated structure. From the results of a least-squares treatment of the $LiYMo_3O_8$ powder data, we are able to present proof of the distribution of Li and Y in the tetrahedral and octahedral sites and somewhat refined values of the position parameters.

Experimental

Preparations.—Two methods were used for the preparation of the scandium compound

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[1] W. H. McCarroll, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **79**, 5410 (1957).

[2] P. C. Donohue and L. Katz, *Nature*, **201**, 180 (1964).

$$\mathrm{Li_2CO_3 + Sc_2O_3 + 4MoO_3 + 2Mo \longrightarrow 2LiScMo_3O_8 + CO_2(g)} \quad (1)$$

and

$$\mathrm{Li_2MoO_4 + Sc_2O_3 + 3MoO_3 + 2Mo \longrightarrow 2LiScMo_3O_8} \quad (2)$$

The components were weighed out in the indicated molar ratios, ground together, pressed into a pellet, and sealed in an evacuated silica capsule. For preparation 1, the pellet was heated under vacuum and the CO_2 removed before the capsule was sealed.

The yttrium compound was prepared as in (1), substituting Y_2O_3 for Sc_2O_3.

The optimum preparation temperatures were about 800° for $LiScMo_3O_8$ and about 700° for $LiYMo_3O_8$. Heating times ranged from 24 to 48 hr.

Diffraction patterns of the products showed MoO_2 impurity lines. These were removed by washing the samples with dilute nitric acid.

Analysis and Density.—Analysis and density measurements were performed on the scandium compound. *Anal.* Calcd. for $LiScMo_3O_8$: Li, 1.5; Sc, 9.6; Mo, 61.5. Found[3]: Li, 1.2; Sc, 12.7; Mo, 58.1. On the basis of a hexagonal unit cell with $a = 5.73$ Å. and $c = 4.94$ Å., the theoretical density is 5.53 g./cc. The density found pycnometrically using CCl_4 as the fluid displaced was 5.40 g./cc.

The discrepancies in observed analyses and densities led us to examine the possibility of impurities in the sample. Excess MoO_2 had been observed in the preparations, but this was removed by dilute HNO_3. However, the diffraction pattern of the Sc_2O_3 used was quite poor, so that small amounts of Sc_2O_3 would not have been observed even if present. It was then found that the dilute HNO_3 used to wash the sample did not dissolve Sc_2O_3. There was thus the clear possibility that excess Sc_2O_3 was present in the analyzed sample. Assuming the high Sc analysis (12.7% *vs.* the theoretical 9.6%) was a result of excess Sc_2O_3, it was determined that for each gram of $LiScMo_3O_8$ there would be 0.059 g. of Sc_2O_3. The theoretical Mo percentage then drops to 58.1, as observed, and the theoretical Li percentage drops to 1.4, still somewhat high. Two additional independent analyses for Li gave results of 1.3 and 1.5, so that the 1.4 figure does fall in the observed range and the sample as a whole could very well be $LiScMo_3O_8$ with about 5–6% Sc_2O_3 impurity.

The density too is consistent with this assumption. Using the theoretical density of 5.53 g./cc. for $LiScMo_3O_8$ and the handbook value of 3.86 g./cc. for Sc_2O_3, the density calculated for the impure sample is 5.40 g./cc., in agreement with that observed. Thus, though the evidence is partly circumstantial, the formula $LiScMo_3O_8$ for the new compound is reasonably well established.

Magnetic Measurements.—Measurements of the magnetic susceptibility of $LiScMo_3O_8$ gave a value of 70×10^{-6} e.s.u./g.-atom of Mo. The paramagnetic susceptibility of one unpaired electron, considering spin contribution only, is 1270×10^{-6} e.s.u.[4] Since a single Mo^{IV} ion would have two unpaired electrons, the low value found is consistent with the idea that the Mo ions form bonded groups with the electrons paired. The behavior is similar to that of the $A_2Mo_3O_8$ compounds. An M.O. treatment has been carried out for a three-ring of Mo^{IV} ions coordinated to thirteen oxygens in the arrangement found for the $A_2Mo_3O_8$ compounds. The calculations lead to the conclusion that the six d electrons of the "metal atom cluster" would be paired in bonding orbitals.[5]

Structure Determination

Slow scan, high resolution X-ray powder patterns were taken of $LiScMo_3O_8$ and $LiYMo_3O_8$ using Cu Kα radiation and a G.E. XRD-5 diffractometer. The patterns were indexed using the following hexagonal cell dimensions: for $LiScMo_3O_8$, $a = 5.73$, $c = 4.94$ Å.; for $LiYMo_3O_8$, $a = 5.79$, $c = 5.16$ Å. Observed intensities were measured by weighing paper tracings of the peaks.

TABLE I

ATOMIC POSITIONS FOR $LiScMo_3O_8$ AND $LiYMo_3O_8$
SPACE GROUP P3m1

		Assumed parameters		Refined parameters[a]	
	Position[c]	*x*	*z*	*x*	*z*
1 Li	1c		0.660		0.714 ± 0.087
1 Y (or Sc)	1b		0.750		0.720 ± 0.002
3 Mo	3d	0.854	0.250	0.8534 ± 0.0004	0.250[b]
1 O(1)	1a		0.490		0.495 ± 0.032
1 O(2)	1c		0.000		−0.005 ± 0.028
3 O(3)	3d	0.500	0.490	0.498 ± 0.010	0.464 ± 0.016
3 O(4)	3d	0.167	0.010	0.167 ± 0.009	0.062 ± 0.013

[a] Refined from $LiYMo_3O_8$ powder pattern. [b] Arbitrary *z*. [c] Position 1a, 0, 0, *z*; 1b, $^1/_3$, $^2/_3$, *z*; 1c, $^2/_3$, $^1/_3$, *z*; 3d, $x, \bar{x}, z$; $x, 2x, z$; $2\bar{x}, \bar{x}, z$.

TABLE II

X-RAY DATA FOR $LiScMo_3O_8$

hkl	d_{obsd}[a]	d_{calcd}[a]	I_{obsd}	I_{calcd}	*hkl*	d_{obsd}[a]	d_{calcd}[a]	I_{obsd}	I_{calcd}
100	5.04	4.96	100	61	500		0.9937		
001		4.94			412	0.9918	0.9921		
101	3.53	3.50	40	45	403		0.9914	6	5
110	2.86	2.86	2	1	304	0.9897	0.9903		
200	2.49	2.48			005		0.9888		
111		2.48	43	41	501	0.9729	0.9729	2	3
002		2.47			105	0.9703	0.9698		
201	2.22	2.22	27	36	420		0.9381		
102		2.21			331	0.9374	0.9380		
210	1.877	1.874	3	4	323		0.9368	8	8
112		1.870			224	0.9360	0.9360		
211	1.754	1.752	37	45	115	0.9339	0.9348		
202		1.750			421		0.9216		
300	1.652	1.653	7	4	502	0.9207	0.9212	5	4
003		1.649			314		0.9197		
301	1.567	1.568	10	11	205	0.9189	0.9186		
103		1.563			413	0.9040	0.9052	1	1
212	1.497	1.495	3	3	511		0.8774	7	7
220	1.434	1.433	8	10	422	0.8765	0.8770		
113	1.431	1.429			404		0.8757		
310		1.377			215	0.8748	0.8748		
221		1.376			503	0.8504	0.8504	4	4
302	1.374	1.375	11	13	305	0.8490	0.8488		
203		1.373			512		0.8386		
311	1.327	1.326	1	1	324	0.8370	0.8375	3	3
400	1.240	1.241			600		0.8273		
222	1.238	1.240	11	9	333	0.8264	0.8264	4	2
213	1.236	1.238			006	0.8240	0.8240		
004	1.232	1.236			430		0.8160		
401	1.204	1.204			601		0.8159		
312	1.201	1.203	3	3	423		0.8152	11	10
104		1.199			414		0.8146		
303	1.168	1.168	2	2	225	0.8138	0.8138		
320	1.139	1.139	2	2	106	0.8116	0.8129		
114	1.136	1.135			431	0.8050	0.8051	4	7
321		1.110			315	0.8042	0.8031		
402	1.109	1.109	10	12	520	0.7938	0.7948	5	4
204	1.107	1.106			116	0.7921	0.7919		
410	1.083	1.083	2	2	521		0.7847		
223	1.082	1.081			602		0.7845	21	32
411	1.057	1.058	2	3	513	0.7838	0.7841		
313		1.056			206	0.7819	0.7820		
322	1.034	1.034	3	3					
214	1.032	1.032							

[a] *d* values after reflection 103 are for Cu Kα_1.

Intensities were calculated using positions corresponding approximately to those expected from a close packing of oxygens with the cations in the voids, though the molybdenum atoms were moved slightly in keeping with the postulated intermetal bonding. These *assumed* positions are listed in Table I. The initial calculations of structure factors were made on an I.B.M. 1620 using a program by Dr. F. R. Ahmed. Single over-all temperature factors, determined graphically,

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(3) The analysis was performed by Ledoux and Company, Teaneck, N. J.

(4) P. Selwood, "Magnetochemistry," Interscience Publishers, New York, N. Y., 1956, p. 245.

(5) F. A. Cotton, *Inorg. Chem.*, **3**, 1217 (1964).

TABLE III

X-RAY DATA FOR $LiYMo_3O_8$

hkl	d_{obsd}^a	d_{calcd}^a	I_{obsd}	I_{calcd}	*hkl*	d_{obsd}^a	d_{calcd}^a	I_{obsd}	I_{calcd}
001	5.21	5.16	41	45	005	1.032	1.032	1	0
100	5.05	5.00	7	7	304	1.021	1.021	2	1
101	3.62	3.59	83	98	403	1.013	1.013		
002	2.59	2.58	12	11	105	1.011	1.011	6	6
111	2.53	2.52	31	31	412	1.007	1.007		
200	2.51	2.51	37	41	500	1.002	1.002	1	1
102	2.297	2.292	2	2	501	0.9831	0.9840	4	4
201	2.257	2.252	31	31	115	0.9722	0.9723	2	1
112	1.927	1.924	1	0	330	0.9645	0.9645	7	7
210	1.894	1.893	4	4	224	0.9627	0.9630		
202	1.799	1.796	56	58	323	0.9557	0.9561	9	7
211	1.778	1.777	23	25	205	0.9545	0.9545		
003	1.722	1.729	2	2	331	0.9481	0.9481		
300	1.670	1.669	3	3	420		0.9471	4	3
103	1.627	1.626	10	9	314	0.9461	0.9457		
301	1.588	1.588	14	13	502	0.9355	0.9344	4	3
212	1.526	1.526	4	3	421	0.9311	0.9316		
113	1.480	1.479	5	5	413	0.9226	0.9230	3	3
220	1.448	1.447	15	14	215	0.9063	0.9064	4	4
203	1.419	1.418	10	6	332	0.9040	0.9035		
302	1.403	1.402	3	3	510		0.8997		
221	1.393	1.393	5	3	404	0.8986	0.8989	5	4
310	1.391	1.390			422	0.8885	0.8892	9	8
311	1.342	1.342	5	4	511	0.8862	0.8867		
004	1.292	1.290	4	4	305	0.8780	0.8782	4	3
213	1.274	1.274	9	8	503	0.8657	0.8661	4	4
222	1.262	1.262	7	5	006	0.8603	0.8602	5	4
400	1.253	1.253	4	3	324	0.8581	0.8585		
104	1.251	1.250			512	0.8499	0.8499	2	2
312	1.224	1.224	3	2	106	0.8479	0.8479		
401	1.218	1.218			333	0.8413	0.8413	5	2
303	1.199	1.199	5	4	225	0.8400	0.8403		
320	1.150	1.150	11	9	600		0.8353		
204	1.147	1.147			414	0.8344	0.8343	5	4
402	1.127	1.127	18	16	423		0.8292		
321	1.125	1.122			315	0.8298	0.8299	4	4
223	1.108	1.107	1	1	206	0.8133	0.8133	17	20
410	1.094	1.094	1	1	431		0.8133		
313	1.081	1.081	3	2	520	0.8018	0.8025	3	5
411	1.069	1.070	7	5	513	0.7971	0.7977		
214	1.067	1.066			405	0.7964	0.7967	6	7
322	1.050	1.050	4	3	602	0.7941	0.7947		
					521	0.7923	0.7930		
					504		0.7916	13	9

[a] *d* values after reflection 212 are for Cu $K\alpha_1$.

were used. Scale factors were chosen so that the sum of the observed intensities equalled the sum of the calculated intensities. For $LiScMo_3O_8$, R', defined as $\Sigma(I_{obsd} - I_{calcd})/\Sigma I_{obsd}$, was 25%; for $LiYMo_3O_8$, R' was 15%. When one notes that these discrepancy factors are based on intensities (discrepancy factors based on structure factors would be smaller), it can be seen that the agreement is quite good. The X-ray powder data are listed in Tables II and III.

For $LiScMo_3O_8$ almost all the peaks were composites of several reflections so that a refinement attempt was considered unrealistic. For $LiYMo_3O_8$, however, the chief lack of resolution arose from the fact that *h*0*l* and 0*hl* reflections, and *hkl* and *khl* reflections, had different intensities but necessarily superposed. Since the amount of superposition was relatively limited, it was considered practical to refine the data for $LiYMo_3O_8$ by using the Busing–Martin–Levy least-squares program adapted for unresolved powder data. The adaptation was prepared by N. Morrow. Although the estimated standard deviations for most of the position parameters is quite large (corresponding generally to 0.2 to 0.3 Å.), the molybdenum parameter is quite reliable (estimated standard deviation less than 0.01 Å.). The refinement is based on ΣpF^2 for each peak, where p is the multiplicity and the sum is over the contributing reflections. The R factor based on ΣpF^2 was 10%. The new positions obtained by the above refinement are also listed in Table I. For the purpose of this calculation, isotropic temperature factors were used for each atom but not refined.

With the same program a test was made of tetrahedral and octahedral site occupancy. The assumed arrangement placed Li^{I} in the tetrahedral sites and the Y^{III} in the octahedral sites; R, as stated above, was 10%. A random distribution of Li^{I} and Y^{III} in the tetrahedral and octahedral sites was tested next; R rose to 22%. Finally, the refinement was tried with Y^{III} in the tetrahedral sites and the Li^{I} in the octahedral sites; R jumped to 47%. Clearly the originally postulated site occupancy was correct.

Summary and Discussion

Chemical analysis, density determination, and the methods of preparation and purification indicate the formula $LiScMo_3O_8$ with some certainty for the lithium–scandium–molybdenum oxide discussed. A structure arrangement in which oxygens are in hexagonal close packing, lithium and scandium are in tetrahedral and octahedral holes, and molybdenums are in octahedra which share edges gives a reasonably good fit between observed and calculated X-ray diffraction intensities of the powdered material. A good fit of X-ray data obtained by least-squares refinement establishes the formula and structure for the related compound, $LiYMo_3O_8$. Although the errors in most of the parameters were still quite large even after refinement, the molybdenum parameter is quite accurately determined and conforms to the tight triangular groupings previously observed in the $A_2Mo_3O_8$ compounds.

Similarities of the X-ray patterns of these compounds with that of one prepared by McCarroll, containing Ga, indicate that $LiGaMo_3O_8$ can also be prepared.

These three compounds resemble the compounds $A_2Mo_3O_8$, with, however, roughly half as long c axes. Magnetic measurements for $LiScMo_3O_8$ indicate Mo–Mo bonding, as was the case for the $A_2Mo_3O_8$ compounds. Presumably, the Y and Ga compounds are similar in this respect, though magnetic measurements on these compounds have not been made.

There are definite similarities between the $AMMo_3O_8$ compounds and MoO_2. The unit cells are much alike.[6] In MoO_2 the unit cell formula is Mo_4O_8. If one Mo^{IV} is removed and two ions with total oxidation number equal to four substituted, one has the unit cell formula $AMMo_3O_8$. In the MoO_2 structure, MoO_6 octahedra are joined by edges to form strings with the metal atoms alternately closer and further from each other. In the $A_2Mo_3O_8$ compounds, and also in the $AMMo_3O_8$ compounds, these strings extend in three directions. The alternation in distances between Mo atoms in these strings results in triangular tight groupings of molybdenum atoms.

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(6) A. Magneli, *Arkiv Kemi, Mineral. Geol.*, **24A**, No. 2, 1 (1947).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Halodicarbaundecaborate(11) Ions

BY FREDERIC P. OLSEN AND M. FREDERICK HAWTHORNE[1]

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Ions of composition $B_9C_2H_{10}R_1R_2^-$ have been reported[2] as the product of alcoholic base on the $B_{10}C_2H_{10}R_1R_2$ carboranes. These ions are precursors to a variety of other compounds including carboranes[3] and organometallic analogs.[4] A route to monohalogenated derivatives of the $B_9C_2H_{10}R_1R_2^-$ ions has now been found.

Experimental

$B_9C_2H_{11}I^-$.—A solution of 5.9 g. of iodine (24 mmoles) in 25 ml. of absolute ethanol was slowly added to a stirred solution of 4.0 g. (24 mmoles) of $KB_9C_2H_{12}$ in 25 ml. of absolute ethanol. The color of the I_2 was rapidly discharged and KI precipitated during the addition. After filtration the ethanolic solution was diluted to 250 ml. with water and excess aqueous tetramethylammonium chloride was added. The solution was cooled to 0° and the tetramethylammonium salt of the monohalogenated ion was separated by filtration. Recrystallization of the crude tetramethylammonium salt from hot aqueous ethanol gave the product as plates in 75% yield. Iodinated derivatives of C-substituted anions were prepared in an identical manner. Replacement of I_2 by Br_2 gave an analogous monobrominated material. Relevant analytical data are presented in Table I. A representative ^{11}B n.m.r. spectrum is shown in Figure 1.

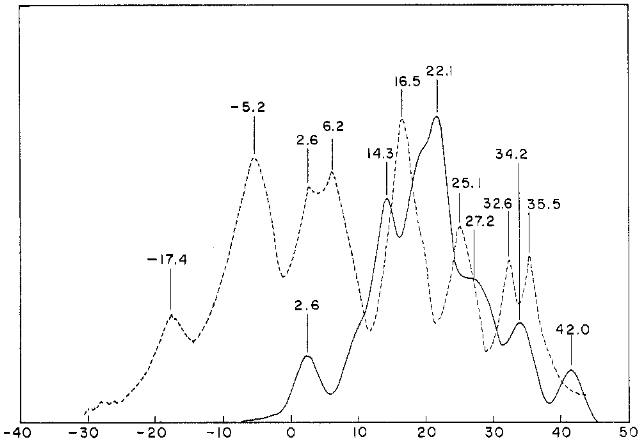

Figure 1.—^{11}B n.m.r. spectra of $(CH_3)_4NB_9C_2H_{11}I^-$ (– – – –) and $B_9C_2H_{12}I$ (———) at 19.3 Mc./sec.

TABLE I

ANALYTICAL DATA FOR $(CH_3)_4N^+B_9H_9C_2R_1R_2X$

R_1	R_2	X	Yield, %	λ_{max}	ϵ	Equiv. wt. Calcd.	Equiv. wt. Found	Calcd, % C	Calcd, % H	Calcd, % N	Calcd, % B	Calcd, % X	Found, % C	Found, % H	Found, % N	Found, % B	Found, % X
H	H	I	75	229	3880	333	340	21.6	6.9	4.2	29.1	38.2	21.7	7.4	3.8	29.0	38.0
H	CH_3	I	78	231	4600	347	348	24.2	7.2	4.0	27.9	36.6	24.4	7.3	4.0	28.1	36.9
H	C_6H_5	I	83	226 255	6140 6230	409	411	35.2	6.6	3.4	23.7	31.1	34.8	7.0	3.1	23.4	30.9
CH_3	CH_3	I	76	231	550	361	371	26.6	7.5	3.9	26.9	35.2	26.5	7.5	4.0	26.8	35.3
CH_3	CH_3	Br	71	225	4100	314	314	30.6	8.6	4.5	30.9	25.5	30.6	8.8	4.7	30.7	25.7

$B_9C_2H_{12}I$.—A solution of $(CH_3)_4N^+B_9C_2H_{11}I^-$ in aqueous acetonitrile was passed through an acidic ion-exchange column and the resulting solution concentrated to dryness. The product was purified by sublimation at 40-50° under high vacuum. Like its unhalogenated analog,[2] the product was both extremely hygroscopic and thermally unstable.[3] The yield of purified product of m.p. 70–71° was about 10%.[5] *Anal.* Calcd. for $B_9C_2H_{12}I$: C, 9.23; H, 4.62; B, 37.4; I, 48.8; equiv. wt., 260. Found: C, 9.26; H, 5.11; B, 36.8; I, 48.8; equiv. wt., 262.

Results and Discussion

Addition of I_2 to an aqueous ethanol solution of $M^+B_9C_2H_{12}^-$ precipitated MI and left the H_3O^+ salt of $B_9C_2H_{11}I^-$ in solution. After the addition of 1 mole of I_2, the reaction was complete and any additional I_2 was not decolorized.

The structure shown in Figure 2 is favored for the product. Evidence in support thereof comes from the ^{11}B n.m.r. spectrum of $B_9C_2H_{12}I$ formed by protonation of $B_9C_2H_{11}I^-$. Electrophilic substitution is expected to occur at the open face of the $B_9C_2H_{12}^-$ ion. Since halogenated C,C′-dimethyl derivatives were obtained, attack at carbon is ruled out. Halogenation of the two types of boron atoms present in the open face would lead to products which may be differentiated on the basis of ^{11}B n.m.r. spectra. Halogenation of the boron atom which lies upon the plane of molecular symmetry would yield a product ion which contained only one doublet of relative intensity 1. Attack at the boron atoms which lie off the plane would make all

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[1] Alfred P. Sloan Research Fellow.

[2] R. A. Wiesboeck and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 1642 (1964).

[3] F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *ibid.*, **86**, 4222 (1964).

[4] M. F. Hawthorne, D. C. Young, and P. A. Wegner, *ibid.*, **87**, 1818 (1965); M. F. Hawthorne and T. D. Andrews, *ibid.*, **87**, 2496 (1965): M. F. Hawthorne and R. L. Pilling, *ibid.*, in press.

[5] The bulk of the material consisted of nonvolatile yellow solids.