charges on the two ions should be equal. In addition, the geometry of the chelate group, in particular the value of the O–Co–N angle, is likely to be the same in both tetrahedral and octahedral complexes. For the complexes of bivalent metals with salicylaldimines it has in fact been shown that the angle O–M–N for the "tetrahedral" complexes is 94°,[13] while for the "square-planar" complexes it is also 94°.[12]

The *trans*-octahedral configuration is also to be assigned to the cobalt(III) complexes with substituted salicylaldimines in which R = C_6H_5, X = H and R = *n*-C_3H_7, X = 3,4-benzo and 5,6-benzo. In fact, the dipole moments of these complexes are very near to those of cobalt(II) with the analogous ligands.

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Hexaborane-12 Isolation and Identification[1]

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Hexaborane-12 has been isolated in a good state of purity by application of gas chromatography to separation of the products from several boron hydride interconversions. Vapor pressures, the melting point, an elementary analysis, infrared spectra, and monoisotopic mass spectra are reported, the latter in comparison with hexaborane-10 and pentaborane-11.

Hexaborane appears in several preparations, but in traces, as first found by Stock,[3] who was prevented by the low plate efficiency of fractional condensation from separating cleanly the substance (B_6H_{12}?). The compound has been identified mass spectrometrically in admixture with hexaborane-10 among products from silent discharge treatment of diborane.[4] It has been found as an intermediate in the shock-tube pyrolysis of diborane[5] and as one product from the treatment of the triboranate anion with acid.[6]

In this laboratory B_6H_{12} was collected by g.l.c. separation in trace amounts from several boron hydride interconversions until a sufficient quantity became available to determine the properties reported here.

Experimental

Vacuum line operations used were those developed by Stock[7] and by Schlesinger and his co-workers and described by Sanderson.[8] The g.l.c. separations were carried out on apparatus designed, constructed, and operated as previously described[9,10] with the helium carrier gas vented at atmospheric pressure. At 25° the relative retention times were: B_2H_6, 11; B_4H_{10}, 34; B_5H_9, 100; B_5H_{11}, 124; B_6H_{12}, 330; B_6H_{10}, 500. A column 35 cm. long × 0.6 cm. diameter charged with mineral oil on firebrick completely resolved the two hexaboranes.

The infrared spectrum was obtained on a Perkin-Elmer Model 21 spectrometer with sodium chloride optics, a 5-cm. cell path, and a gas pressure of about 2 cm. Atmospheric absorption peaks were used for calibration to establish the scale within 5 cm.$^{-1}$.

The mass spectra were obtained with a Consolidated Model 20-103 mass spectrometer using a rhenium filament. To ensure a faithful cracking pattern the instrument was checked with pentaborane-11[10] before each run. Ionizing voltages of 70 and 8–14 v. were used. Owing to the uncertainty often experienced in observing mass spectra of certain boron hydrides at the full ionizing potential, 70 v., mass spectra from triplicate samples of hexaborane-12 were given rough statistical analysis with the finding that the standard deviation from the mean abundance for each mass number was ±2.5% for forty mass numbers. The isotopic ratio $B^{11}/B^{10} = 4.00$ was used, as is customary,[11] to reduce the polyisotopic abundances to the monoisotopic values. The residuals were calculated for the monoisotopic reduction using the formula $R = (\Sigma N_i^2)^{1/2}/\Sigma I$, where R is the residual, N_i is the residue for the ith group, and I, the intensity, is summed over all the abundances.

Hexaborane-12 was obtained in yields of about 1% of the boron in the following reactions: (1) preparation of pentaborane-11 from tetraborane and diborane in a static system at 110° for 10 min.; (2) reaction of tetraborane and diborane and the pyrolysis of tetraborane in the hot–cold reactor[12] with the hot side at 110° and the cold side at 0°; (3) the decomposition of liquid pentaborane-11 at 25°, the easiest systematic method. The large excess of pentaborane-11 over products makes a quantitative determination of yield impossible. Gas chromatographic assay showed about 12% of starting material to disappear in 3 hr. Diborane, tetraborane, and hexaborane-12 appeared in amounts of about 2, 3, and 1.5%, respectively. Initial addition of an equivalent amount of diborane at 10 atm. pressure increased the tetraborane and hexaborane-12 yields inappreciably. No hexaborane-12 was

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(2) Postdoctorate fellow, 1962–1963.

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Table I

Vapor Pressures of B_6H_{12}

Temp., °C.	−30.7	−23.6	−13.5	−7.3	0	5.2
p, mm.	2.6	3.8	7.1	10.5	17.1	22.8

Table II

Reactions of Hexaborane-12

	B_6H_{12}, mmole		Products, mmole × 10^3			
Expt.[a]	Reactant	Recovered	B_2H_6	B_4H_{10}	B_5H_9	B_5H_{11}
1	0.185	0.182	*b*	*b*	0	0.5
2	0.75	0.71	2.1	0.85	0	1.4
3	0.25	0.11	. . .	2.2	0	6.2
4	0.56	0.40	11.5	3.1	12.9	10.5
5	0.95	0.69	48.6	54.3	63.0	80.0

[a] For conditions see Text. [b] Trace.

obtained in the following trials: (1) pentaborane-11 and diborane at 110° for 30 min., instead the products were some pentaborane-9 and tetraborane; (2) tetraborane at 110° for 5 min., instead diborane, pentaborane-11, and pentaborane-9 were products together with solid hydrides; (3) decomposition of pentaborane-11 in the hot–cold reactor with a differential temperature of 110 to −35°.

The melting point was determined in a dropping plunger device[7,8] using a freshly chromatographed sample. The values found were −82.2 and −82.3°. After the two measurements the rechromatographed sample contained ~0.4 mole % diborane as the only impurity detectable on the gas chromatograph.

The apparatus[13] for analysis was designed to serve for weighing and for pyrolysis. It consisted of a ten-turn spiral, 3 cm. o.d. × 8 cm. long, constructed from 6-mm. o.d. Vycor tubing. The entry tube passed through the center to form a loop extending 8 cm. below, where the sample was condensed. After the sample weighing an initial amount of hydrogen (0.02 mmole) was removed to facilitate recondensing the sample in the loop. The pyrolysis was carried out by heating the spiral in a furnace initially at 800°, finally at 900°, while the sample was slowly vaporized. The hydrogen was removed by a Toepler pump as soon as it was formed to minimize diffusion through the hot Vycor tubing. Finally the furnace was lowered to heat the bottom of the spiral at the maximum temperature. A sample weighing 25.20 mg. gave 1.955 mmoles of hydrogen and 21.28 mg. of boron. *Anal.* Calcd. for B_6H_{12}: H, 15.7; B, 84.3. Found: H, 15.6; B, 84.4.

The vapor pressures were observed on freshly chromatographed

Table III

Polyisotopic Mass Spectra of the Hexaboranes

	B_6H_{10}	B_6H_{12}	
Mass no.	11 v.	11 v.	70 v.
78		1.5	0.8
77		11.8	5.3
76	67.1	75.6	29.1
75	100.0	100.0	39.0
74	86.7	89.7	56.2
73	58.1	65.3	59.2
72	48.9	45.0	92.7
71	41.3	29.9	100.0
70	23.1	15.4	72.1
69	8.4	5.6	47.4
68	2.2	1.6	35.1
67	0.4	0.3	34.0
66			29.6
65			17.1
64	0.7	30.1	23.1
63	1.0	37.7	22.7
62	0.7	39.1	38.8
61	0.5	30.5	40.2
60	0.4	18.0	63.7
59	0.5		77.3
58	0.5	3.8	63.7
57		1.3	52.8
56		0.6	43.9
55			39.9
54			25.8
53			10.3
52		1.0	3.0
51		1.2	1.5
50		15.3	14.3
49		15.5	22.9
48		10.9	44.0
47		6.3	51.4
46		2.3	40.5
45		30.6	26.6
44			15.7
43			7.4
42			2.2
41			1.4
40			0.3
39			9.8
38			12.0
37			14.7
36			17.4
35			18.3
34			11.3
33			4.8
32			1.5
31			0.4
30			0.1
29			0.9
28			0.9
27			12.2
26			9.5
25			8.2
24			11.7
23			6.6
22			2.5
21			0.6
20			0.1
Doubly Charged Ions			
$36^1/_2$			0.3
$35^1/_2$			0.2
$34^1/_2$			0.2
$33^1/_2$			0.2
$32^1/_2$			0.04
$29^1/_2$			0.05
$28^1/_2$			0.1
$27^1/_2$			0.03

TABLE IV

MONOISOTOPIC MASS SPECTRUM OF HEXABORANE-12 AT 70 V.

Positive ion species	Relative abundances	Positive ion species	Relative abundances
B_6H_{12}	1.4	B_4H_5	16.0
B_6H_{11}	7.3	B_4H_4	52.9
B_6H_{10}	39.8	B_4H_3	30.8
B_6H_9	2.9	B_4H_2	20.2
B_6H_8	56.6	B_4H	12.2
B_6H_7	5.9	B_4	6.0
B_6H_6	100.0	Mass 43–40	0
B_6H_5	4.3	B_3H_6	17.4
B_6H_4	23.0	B_3H_5	8.3
B_6H_3	13.9	B_3H_4	16.7
B_6H_2	13.0	B_3H_3	16.8
B_6H	20.2	B_3H_2	16.8
B_6	4.6		
Mass 65	0	B_3H	4.2
B_5H_9	29.6	B_3	2.0
B_5H_8	1.6	Mass 32–30	0
B_5H_7	48.0	B_2H_7	1.6
B_5H_6	7.1	Mass 28	0
B_5H_5	73.4	B_2H_5	21.1
B_5H_4	35.8	B_2H_4	6.6
B_5H_3	21.4	B_2H_3	0
B_5H_2	33.5	B_2H_2	15.4
B_5H	14.9	B_2H	4.1
B_5	27.3	B_2	2.5
Mass 54–52	0	Mass 21–20	0
B_4H_7	3.0		
B_4H_6	23.9	$R = 2.5 \times 10^{-3}$	

samples in a static system with a liquid phase cooled by fixed temperature slush baths; the temperatures were measured by a vapor pressure thermometer, and the pressures were observed with a cathetometer. The values, scarcely so numerous as to justify an equation, are given in Table I. The sample was lost during transfer for rechromatographing, but a similar one, giving the same zero tension over a period of 10 min., was found to contain ~0.5 mole % diborane as the only impurity detectable on the gas chromatograph. The Clapeyron–Clausius plot is strictly linear in the range +5 to −14°, and below this a slight curvature finds the pressure 0.2 and 0.5 mm. above the straight line at −23.6 and −30.7°, respectively.

Some reactions of hexaborane-12 were observed on a 0.2–0.5 mmole scale with gas chromatographic monitoring. The results are given in Table II for decompositions at 25° (1) of vapor for 1 hr.; (2) of liquid; (3) of liquid with an equivalent amount of diborane at 10 atm. pressure, each for 3 hr.; and for reactions at 95° for 10 min. (4) of decomposing vapor; and (5) of vapor with hydrogen gas at 43 cm. pressure. The decompositions all gave hydrides higher than B_6, mostly nonvolatile. For this reason material balances were not obtained.

Results and Discussion

The identification of hexaborane-12 rests upon its separation by gas chromatography (efficiency about 300 equivalent theoretical plates), the sharp closely reproducible melting point, an ultimate analysis, and a polyisotopic mass spectrum reducible to the monoisotopic representation with a residual as low as $R \cong 10^{-3}$. The mass spectrum furnishes (a) a molecular weight through absence of masses higher than the parent peak, (b) a chemical analysis through reduction to the monoisotopic spectrum with a residual as low as 10^{-3}, and (c) an additional demonstration of purity through (a) and (b).

TABLE V

MONOISOTOPIC SPECTRA OF THE HEXABORANES AT 11 V.

Positive ion species	B_6H_{12}	B_6H_{10}
B_6H_{12}	2.5	
B_6H_{11}	16.0	
B_6H_{10}	100.0	100.0
B_6H_9	1.6	0.2
B_6H_8	48.7	35.4
B_6H_7	2.5	2.5
B_6H_6	19.5	30.6
B_6H_5	2.6	1.9
B_6H_4	0	0.2
B_6H_3	0.4	0.5
B_5H_9	59.9	0.2
B_5H_8	0.2	1.1
B_5H_7	40.0	0.1
B_5H_6	1.2	0.4
B_5H_5	8.1	0
B_5H_4	1.1	0.6
B_5H_3	0.1	
B_5H_2	0.5	
B_5	0.4	
B_4H_8	2.0	
B_4H_7	0.4	
B_4H_6	29.4	
B_4H_5	1.2	
B_4H_4	9.5	
B_4H_3	0.7	
B_4H_2	0.2	
R	10^{-3}	10^{-3}

The polyisotopic spectra of hexaborane-12 at 70 and 11 v. are found in Table III. Also included is the spectrum at 11 v. for hexaborane-10. These can be found reduced to the partial monoisotopic spectra in Tables IV and V. For use in interpreting the spectra, reference has been made to similar results for pentaborane-11,[10] pentaborane-9,[14] and hexaborane-10 at 70 v.[15]

Mass spectra for the two hexaboranes show similar cracking patterns for the parent molecules at both 70 and 11 v., but the parent boron skeletons are cracked differently. At 70 v. hexaborane-12 undergoes fragmentation to B_5 and B_4 species to about five times greater degree than does hexaborane-10. On the average, pentaborane-11 is fragmented about twice more than pentaborane-9. In each case, the most abundant species among the skeletal fragments are those represented by $(B_nH_n^+)$. Such similarities become even more apparent at 11 v. ionizing potential where hexaborane-10 undergoes no observable skeletal fragmentation. Both dihydroboranes are shattered at 11 v., hexaborane-12 to give $(B_5H_9^+) > (B_5H_7^+)$ and pentaborane-11 to give $(B_4H_8^+)$, though in this case $(B_4H_6^+)$ has the greater abundance. Nevertheless, each has a structure which can be altered by removal of a BH_3 fragment.

The principal bands observed in the infrared spec-

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Table VI

Infrared Spectra of Hexaboranes and Pentaboranes

	B_6H_{12}		B_6H_{10}		B_5H_{11}		B_5H_9	
Assignment	ν, cm.$^{-1}$	I	ν, cm.$^{-1}$	I	ν, cm.$^{-1}$	I	ν, cm.$^{-1}$	I
BH							2610	s
			2575	s			2598	s
BH_2	2570	s			2548	s		
	2490	s			2460	s		
	2308	w			2312	w		
Bridge	1990	m			2040	m		
	1930	m	1940	m	1940	w		
Bridge					1859	w	1844	w
							1802	m
	1747	w						
	1627	w					1621	m
			1547	m				
Bridge	1491	s	1480	s	1435	m	1449	m
	1393	m			1405	m	1413	m
	1356	m						
BH_2	1164	s			1164	s		
B–H							1126	w
BH	1055	s			1043	m		
	1023	s			1020	w		
BH_2	942	m			951	m		
BH_2					899	w		
	891	m	884	m				
	833	w					799	w
	755	s	759	s				
	747	s	748	s				
	702	m			703	w		
			698	sh				
Skeleton	682	m	690	w				
			668	sh				
Skeleton							628	s
Skeleton							616	s
Bridge							605	s
							568	w

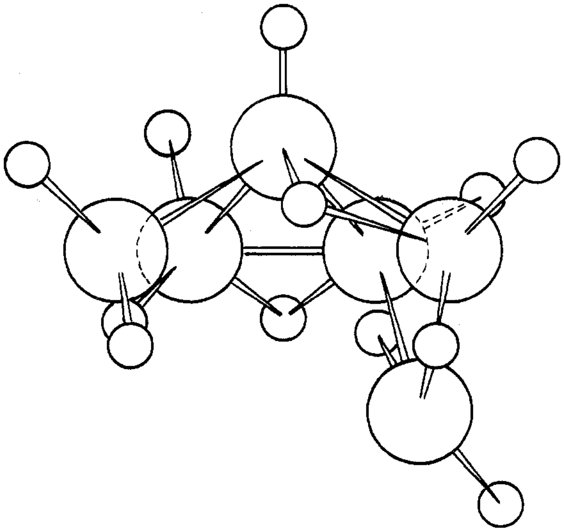

Figure 1.

trum of hexaborane-12 are listed in Table VI, together with characteristic bands from hexaborane-10,[14,15] pentaborane-11,[10,16,17] and pentaborane-9[17] for comparison using assignments made in the references cited. The spectra of hexaborane-12 and pentaborane-11 have in common all the strong BH_2 frequencies and some BH and bridge frequencies. In addition, hexaborane-12 has some bridge frequencies which may arise from framework vibrations.

Chemically, hexaborane-12 has a stability which is the greater, the purer the sample. Since other boron hydrides induce its decomposition, the substance can be considered very reactive rather than intrinsically unstable. Particularly significant are reactions 4 and 5 of Table II, where hydrogenation is seen to give increased amounts of lower hydrides.

A survey of the physical and chemical data shows a resemblance between hexaborane-12 and pentaborane-11. The plane topological projection of the 4212 structure[18] confirmed by B^{11} n.m.r.[6] obscures this relation, but in three dimensions it becomes more apparent. Figure 1 is a face-on view of the proposed conformation based upon an elaboration of the pentaborane-11 structure in which a borane group has been inserted at one side hydrogen bridge location with the sixth boron atom at those B–B distances found on the side of the pentaborane-11 pyramid. The molecule is a "boranated" pentaborane-11 in the same sense that pentaborane-11 is a "boranated" tetraborane. The reactivity of hexaborane-12 with diborane makes observation of the "boranation" reaction difficult, but the reversal is seen in the reaction with hydrogen.

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