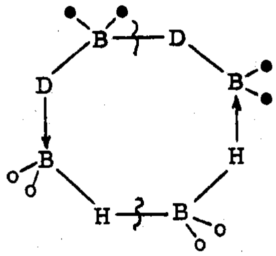
Finally, we reanalyzed Maybury and Koski's[8] data on

$$B_2H_6 + B_2D_6 \rightleftarrows 2H_3B{\cdot}BD_3 \qquad [K_9 \simeq 4] \tag{9}$$

They reported an activation energy of 21.8 ± 3 kcal mol^{-1} and a total order of $^3/_2$. These two results are incompatible. If their proposed mechanism applied (dissociation + three-center displacement) the activation energy would have been (18 + 10) kcal mol^{-1}. Furthermore, their observed exchange rate would have been slower, being limited by the low steady state concentration of borane. We propose that (within their experimental error) their data can be fitted to an overall order of two, with

$$k_{9f} \simeq 10^{15} \exp[-7675 \pm 110/T] \qquad \mathrm{mol^{-1}\,cm^3\,s^{-1}}$$
$$k_{9r} \simeq 10^{14} \exp[-7675 \pm 110/T] \qquad \mathrm{mol^{-1}\,cm^3\,s^{-1}}$$

Here one may postulate an eight-atom ring for the transition state,[11]



As mentioned previously,[7] there is experimental evidence for the existence of single –H– bridges between two boron atoms. Also, one can account for the facile production of B_4H_{10} from B_2H_6 via this transition state, which merely has to lose H_2 in a transannular elimination.

It is interesting to note that unlike these fast reactions, the rate of the homogeneous exchange between B_2H_6 and D_2 is in doubt;[9] that for ($H_3BCO + D_2$) is also unknown. In contrast, Curtis and Porter[10] reported a fast bimolecular rate for

$$HBF_2 + D_2 \rightleftarrows DBF_2 + HD \qquad [K_{10} = 4.22 \pm 0.1] \tag{10}$$
$$k_{10f} \simeq 10^{16} \exp[-8900/T] \qquad \mathrm{mol^{-1}\,cm^3\,s^{-1}}$$
$$k_{10r} \simeq 5 \times 10^{14} \exp[-9100/T] \qquad \mathrm{mol^{-1}\,cm^3\,s^{-1}}$$

Here a pentacoordinated boron atom characterizes the transition state.

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Registry No. H_3BCO, 13205-44-2; PF_3, 7783-55-3; B_2H_6, 19287-45-7; H_3BPF_3, 14931-39-6.

References and Notes

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(2) K-R. Chien and S. H. Bauer, *J. Phys. Chem.*, **80**, 1405 (1976).
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(4) (a) M. E. Garabedian and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 176 (1964); (b) A. B. Burg and Y. C. Fu, *ibid.*, **88**, 1147 (1966).
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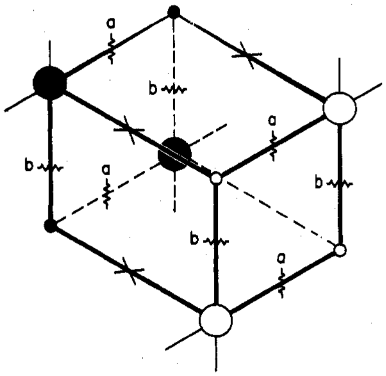
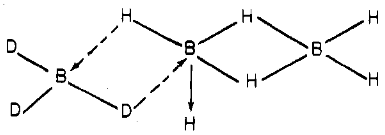
(7) Such structures have been proposed for various B/H compounds: R. E. Williams, H. D. Fisher, and C. O. Wilson, *J. Phys. Chem.*, **64**, 1583 (1960); D. F. Gaines, *Inorg. Chem.*, **2**, 523 (1963); R. E. Dickerson and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 212 (1957).
(8) P. C. Maybury and W. S. Koski, *J. Chem. Phys.*, **21**, 742 (1953).
(9) Summary presented by J. D. Odom and R. Schaeffer, "Progress in Boron Chemistry", Vol. 2, R. J. Brotherton and H. Steinberg, Ed., Pergamon Press, Oxford, 1970, Chapter 4. The difficulty with Koski's data for the H/D exchange reaction between B_2H_6 with D_2 was not removed by R. A. Marcus' analysis [*J. Chem. Phys.*, **23**, 1107 (1955)] and the subsequent study by J. S. Rigden and W. S. Koski [*J. Am. Chem. Soc.*, **83**, 3037 (1961)]. We find it unreasonable that at 55 °C borane and D_2 attain a rapid equilibrium and that the overall exchange rate is limited by the rate of $H_2BD + B_2H_6 \rightarrow H_2DB{\cdot}BH_3 + BH_3$.
(10) P. M. Curtis and R. F. Porter, *Chem. Phys. Lett.*, **37**, 153 (1976).
(11) **Note Added in Proof.** Professor R. T. Paine, Jr. (University of New Mexico) proposed a cage structure for this transition state which is quite appealing, based on pentacoordinated boron atoms.



Exchanges occur upon approach of two diboranes along the →← path and then receed after cleavage either at the a∼∼ or b∼∼ bonds, thereby leading to exchange. Through the cage transition state, or via the 8-atom ring, the BH_3 units remain intact, such that in a double labeled experiment [$^{11}B_2D_6 + {}^{10}B_2H_6$], the rates of exchange of the $^{10}B/^{11}B$ and of the H/D are the same. In both cases the breaking away of a borane unit from the B_4H_{12} would be a less likely event, so that unequal B/H scrambling would be slower than borane exchange. On the other hand were the borane displacement to occur via four atom bridges



the integrity of the $^{11}BD_3$ or $^{10}BH_3$ would not be maintained.

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Preparation and Properties of Selenaboranes and Telluraboranes

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In aqueous ammonia Na_2Se_4 and Na_2Te_4 react with decaborane(14) to give $B_{10}H_{11}Se^-$ and $B_{10}H_{11}Te^-$, respectively. These anions form $B_{10}H_{12}Se$ and $B_{10}H_{12}Te$ upon acidification. The electron rich compound $B_9H_9Se_2$ is formed as a by-product in the reaction of polyselenide ion with decaborane. Treatment of $B_{10}H_{12}Se$ or $B_{10}H_{12}Te$ with aqueous KOH and $CoCl_2$ or $FeCl_2$ forms $Co(B_{10}H_{10}E)_2^{2-}$ and $Fe(B_{10}H_{10}E)_2^{2-}$ (E = Se or Te), respectively. Triethylamine, cyclopentadiene monomer, $CoCl_2$, and $B_{10}H_{12}Se$ or $B_{10}H_{12}Te$ in tetrahydrofuran solution form $(C_5H_5)Co(B_{10}H_{10}Se)$ and $(C_5H_5)Co(B_{10}H_{10}Te)$, respectively.

The first synthesis of polyhedral thiaboranes was reported nearly a decade ago.[1] To date this chemistry has not been extended to polyhedral insertion of other elements of group 6. This is probably due to the known malodorous and poi-

Table I. Analyses, Melting Point, and Molecular Weight Data for Selena- and Telluraboranes

Compd	Anal, %						Mp, °C	Mol wt[a]	
	Calcd			Found					
	C	H	Metal	C	H	Metal		Calcd	Found
$B_{10}H_{12}Se$ (I)		6.08			5.90		239–241 dec	202	200
$B_9H_9Se_2$ (II)		3.43			3.61		340–342	272	266
$B_{10}H_{12}Te$ (III)		4.88			5.03		244–246 dec	252	242
$[N(CH_3)_4]_2[Fe(B_{10}H_{10}Se)_2]$ (VI)	16.06	7.41	9.33	16.13	7.38	8.13			
$[N(CH_3)_4]_2[Fe(B_{10}H_{10}Te)_2]$ (VII)	13.81	6.38	8.03	13.23	6.31	8.33			
$N(CH_3)_4[Co(B_{10}H_{10}Se)_2]$ (VIII)	9.11	6.12	11.17	9.06	6.15	11.73			
$N(CH_3)_4[Co(B_{10}H_{10}Te)_2]$ (IX)	7.69	5.16	9.43	8.53	5.31	10.44			
$(C_5H_5)Co(B_{10}H_{10}Se)$ (X)	18.70	4.71	18.35	18.65	4.84	18.54	268–269		
$(C_5H_5)Co(B_{10}H_{10}Te)$ (XI)	16.24	4.09	15.94	16.45	4.15	15.18	290.5–292		

[a] Osmometric molecular weight in benzene.

Table II. Infrared Data

Compd	Absorption, cm^{-1}
I	2565 vs, 1400 w, 1082 w, 1014 s, 981 s, 928 m, 906 w, 871 w, 860 m, 767 m, 710 m, 700 m, 640 w, 527 w, 470 w
II	2590 vs, 2555 vs, 1400 w, 997 s, 974 s, 906 m, 880 w, 857 w, 819 w, 783 m, 766 m, 739 w, 692 w, 563 w, 500 w
III	2582 s, 2550 vs, 1400 w, 1079 m, 1010 s, 970 s, 921 m, 900 w, 855 w, 827 w, 766 m, 720 w, 698 w, 637 w, 460 w
IV	3035 w, 2530 vs, 1480 s, 1418 m, 1292 m, 1057 m, 1017 m, 988 m, 948 s, 912 m, 874 w, 861 w, 750 w, 739 w, 690 w, 492 w
V	3032 w, 2500 vs, 1477 s, 1413 m, 1325 m, 1052 m, 1012 m, 989 m, 948 s, 903 m, 852 w, 758 w, 738 w, 540 w, 490 w
VI	3040 m, 2550 vs, 2500 vs, 2445 s, 2418 s, 1483 s, 1447 w, 1412 m, 1291 w, 1171 w, 1072 w, 1012 s, 948 m, 889 m, 881 m, 868 w, 769 m, 732 w, 691 w, 521 w, 462 w
VII	3035 m, 2530 vs, 2500 vs, 2435 s, 2410 s, 2390 s, 1483 s, 1448 w, 1411 m, 1291 w, 1170 w, 1070 w, 1012 s, 948 m, 923 w, 887 m, 870 w, 860 w, 761 m, 735 m, 506 w
VIII	3037 w, 2580 s, 2525 vs, 2480 sh, 1481 s, 1417 w, 1008 s, 948 m, 912 w, 893 m, 820 w, 758 m, 724 m, 709 w, 612 w
IX	3032 w, 2565 s, 2520 vs, 2455 s, 1481 s, 1416 w, 1285 w, 1062 w, 1006 s, 943 m, 915 w, 889 m, 860 w, 820 w, 780 w, 760 m, 726 m, 709 w, 610 w, 510 w
X	3120 m, 2580 s, 2560 s, 2530 s, 2505 s, 1429 m, 1418 m, 1068 w, 1012 s, 1000 m, 931 w, 907 w, 889 w, 846 s, 812 w, 760 w, 722 m, 685 w, 560 w, 523 w
XI	3115 m, 2560 s, 2542 s, 2502 s, 1427 m, 1417 m, 1065 w, 1006 s, 902 s, 929 w, 901 w, 882 w, 842 s, 810 w, 760 w, 720 m, 510 w

Table III. Electronic Spectra of the Metal Derivatives

Compd[a]	λ_{max}, nm (ϵ)
VI	532 (56), 426 (39), 285 (11 000), 261 (12 600), 230 (12 300)
VII	551 (43), 399 (783), 272 (7260)
VIII	439 (366), 318 (12 800), 225 (4900), 195 (7060)
IX	479 (33), 319 (14 800), 222[b] (14 200)
X	473 (397), 290 (21 300), 244 (7270), 205 (9390)
XI	444 (366), 295 (15 700), 211 (10 400)

[a] Acetonitrile solution. [b] Shoulder.

sonous character of many selenium and tellurium compounds and to the expectation of a chemistry very similar to that of the sulfur analogues. We report here the preparation of the first selena- and telluraboranes which prove to have some novel chemistry of their own.

Experimental Section

Boron (^{11}B) NMR spectra were obtained at 70.6 MHz with a Varian HR-220 spectrometer and were externally referenced to $BF_3{\cdot}O(C_2H_5)_2$. Proton spectra were measured with a Varian EM-360 spectrometer with acetone-d_6 solvent. Elemental analyses and osmometric molecular weight determinations (summarized in Table I) were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Infrared spectra (see Table II) were obtained as KBr disks employing a Perkin-Elmer 467 spectrometer. Low-resolution mass spectra were obtained with an Atlas CH-7 instrument and high-resolution mass spectra with an AEI MS-9 instrument. Ultraviolet–visible spectra (see Table III) were measured with a Cary 14 instrument. Melting points were obtained in evacuated sealed capillaries and are uncorrected.

$B_{10}H_{12}Se$ (I) and $B_{10}H_{12}Te$ (III). A 500-mL, three-neck flask was fitted with a dry ice condenser and an overhead stirrer. Ammonia, 150 mL, was condensed, under nitrogen, into the flask, after which 3.80 g (0.165 g-atom) of sodium metal was added in small chips. Elemental selenium, 26.00 g (0.329 g-atom), was added through a solid addition tube over a 45-min period, due to the sputtering caused by the vigorous reaction during the formation of sodium polyselenide. The reaction was stirred for 2 h before the ammonia was evaporated to a volume of approximately 50 mL. Deoxygenated water, 250 mL, was added and the mixture stirred a few minutes before $B_{10}H_{14}$, 10.00 g (0.077 mol), was added gradually over a 30-min period. The reaction mixture was stirred at room temperature for an additional 22 h.

An insoluble material containing $B_9H_9Se_2$ (compound II) was removed from the solution by filtration. Excess saturated tetramethylammonium iodide solution was added to the filtrate and the resulting solid was collected by filtration and washed with water. The salt was extracted from the filter with acetone and evaporation of the acetone solution yielded 15.6 g of crude $N(CH_3)_4(B_{10}H_{11}Se)$ (compound IV).

The salt was dissolved in a minimum of acetonitrile and filtered to remove insoluble impurities. The filtrate was placed in a 250-mL separatory funnel and 20 mL of concentrated HCl added. The resulting solution was extracted with 150-mL portions of a diethyl ether/hexane mixture (1:2 ratio) until no further material was obtained in the extract. The extracts were evaporated to dryness under vacuum and the resulting solid was sublimed at 50–60 °C (approximately 0.1 mm). Crystallization of the sublimate from hexanes yielded 7.5 g (49% yield) of I. The low-resolution mass spectrum cutoff at *m/e* 202 corresponds to the $^{11}B_{10}H_{12}{}^{80}Se$ ion.

Compound III, $B_{10}H_{12}Te$, was obtained by the same procedure. The crude product was sublimed at 50–70 °C (0.1 mm) and the sublimate crystallized from hexanes, producing III in 79% yield.

B_9H_9Se (II). The initial insoluble material in the preparation of I, above, was washed with water, air-dried, and sublimed at 45 °C (0.1 mm) to give 1.02 g (5% yield) of crystalline II. An analytical sample was obtained by recrystallization from hexane.

$N(CH_3)_4[B_{10}H_{11}Se]$ (IV) and $N(CH_3)_4[B_{10}H_{11}Te]$ (V). Crude samples of IV were obtained during the preparation of I; however, analytical samples of IV were obtained by the conversion of $B_{10}H_{12}Se$ to $N(CH_3)_4B_{10}H_{11}Se$.

Pure $B_{10}H_{12}Se$, 0.506 g (0.0025 mol), was dissolved in 20 mL of 15% potassium hydroxide solution. Excess, saturated tetramethylammonium iodide solution was added and the resulting solid was filtered from the solution, washed with water, and vacuum-dried to give 0.66 g (97% yield) of $N(CH_3)_4[B_{10}H_{11}Se]$.

Analytical samples of $N(CH_3)_4[B_{10}H_{11}Te]$ were obtained by the same procedure in similar yield. Both of these samples contain a singlet resonance at 3.46 ppm in the ^1H NMR spectrum due to the $(CH_3)_4N^+$ ion.

$[N(CH_3)_4]_2[(B_{10}H_{10}Se)_2Fe]$ (VI). $B_{10}H_{12}Se$, 0.400 g (0.0020 mol), was added to 75 mL of 33% potassium hydroxide solution in a 250-mL flask fitted with a magnetic stirrer. A solution of $FeCl_2{\cdot}6H_2O$, 2.00 g (0.0122 mol), dissolved in a minimum of water was added to the reaction flask and the reaction mixture was stirred for 44 h. The solution was filtered and the solid by-product was washed with water. Excess, saturated tetramethylammonium iodide solution was added to the burgundy filtrate. The resulting precipitate was filtered from the solution and air-dried. Crystallization from acetone/methanol yielded 0.121 g (8% yield) of $[N(CH_3)_4]_2[(B_{10}H_{10}Se)_2Fe]$ as purple needles.

$[N(CH_3)_4]_2[(B_{10}H_{10}Te)_2Fe]$ (VII). A solution of 33% potassium hydroxide, 160 mL, was prepared with deoxygenated water under nitrogen in a 250-mL, three-neck flask fitted with a magnetic stirrer. $B_{10}H_{12}Te$, 0.400 g (0.001 61 mol), was added to the potassium hydroxide solution and was stirred until it dissolved. A solution of $FeCl_2{\cdot}6H_2O$, 6.0 g (0.026 mol), in a minimum of deoxygenated water was added to the reaction flask. The reaction mixture was stirred under nitrogen for 24 h. The solid by-product was removed by filtration in the air and washed with water until the washings were colorless. Excess, saturated tetramethylammonium iodide solution was added to the burgundy filtrate. The resulting green precipitate was filtered from the solution, washed with water, and extracted with acetone. Approximately 15 mL of water was added to the acetone extract and the resulting solution rotary-evaporated. The fine green crystals were filtered and vacuum-dried to give 0.332 g, 30% yield, of impure VII.

Analytical samples were prepared by placing an acetonitrile solution of VII over sodium amalgam before crystallization from acetonitrile under oxygen-free conditions.

$N(CH_3)_4[(B_{10}H_{10}Se)_2Co]$ (VIII) and $N(CH_3)_4[(B_{10}H_{10}Te)_2Co]$ (IX). A solution of 50% sodium hydroxide, 15 mL, was added to a 50-mL flask fitted with a magnetic stirrer. A 10% sodium hydroxide solution, 5 mL, was used to dissolve $B_{10}H_{12}Se$, 0.45 g (0.0022 mol), before addition to the reaction flask. A solution of $CoCl_2{\cdot}6H_2O$, 1.63 g (0.006 84 mol), in a minimum of water, was added to the reaction flask and the resulting mixture was stirred for 2 h. Oxygen was bubbled through the solution a few minutes before the solid by-product was removed by filtration and washed with water. Excess, saturated tetramethylammonium iodide solution was added to the filtrate and the resulting precipitate collected, washed with water, and air-dried. The salt was chromatographed on a 30 cm × 2 cm alumina column using acetone as eluent. The major yellow band eluted was evaporated to dryness under vacuum and crystallized from ethanol to give 0.168 g (14% yield) of $N(CH_3)_4[(B_{10}H_{10}Se)_2Co]$ as orange needles.

A similar procedure was used in the preparation of $N(CH_3)_4[(B_{10}H_{10}Te)_2Co]$ but the purification procedure was as follows. The crude product was placed on a 19 cm × 2 cm alumina column and was eluted with acetone. The main, fast-moving, band eluted was evaporated to dryness under vacuum. The resulting solid was washed with 95% ethanol before crystallization from acetone/ethanol yielding 0.131 g (10% yield) of $N(CH_3)_4[(B_{10}H_{10}Te)_2Co]$ as orange crystals.

$(C_5H_5)Co(B_{10}H_{10}Se)$ (X) and $(C_5H_5)Co(B_{10}H_{10}Te)$ (XI). Dry tetrahydrofuran, 40 mL, was placed in a three-neck, 100-mL flask fitted with a nitrogen inlet, reflux condenser, and magnetic stirrer. Triethylamine, 5.0 mL, was added to a flask and stirred a few minutes before freshly cracked cyclopentadiene, 1.6 mL (~0.020 mol), was added. Anhydrous cobalt(II) chloride, 1.00 g (0.0077 mol), was then added and the resulting mixture stirred for 22 h. Oxygen was bubbled through the reaction mixture for 30 min before the solvent was removed by rotary evaporation. The crude product was chromatographed on a 18 cm × 2 cm silica gel column and eluted with hexanes/methylene chloride (1:1 ratio). The yellow band eluted was rotary-evaporated and the resulting solid was crystallized from dichloroethane/heptane yielding 0.152 g (12% yield) of $(C_5H_5)Co(B_{10}H_{10}Se)$ as yellow crystals. The ^1H NMR spectrum contains a singlet at 5.87 ppm due to the C_5H_5 group. The low-resolution mass spectrum cutoff at *m/e* 326 corresponds to the $H_{15}{}^{11}B_{10}{}^{12}C_5{}^{57}Co^{82}Se$ ion.

A similar procedure was used in the preparation of $(C_5H_5)Co(B_{10}H_{10}Te)$, with the exception that the reaction time was 20 h. Crystallization from dichloroethane yielded 0.425 g (56% yield) of $(C_5H_5)Co(B_{10}H_{10}Te)$ as yellow needles. The ^1H NMR spectrum contains a singlet at 5.73 ppm due to the C_5H_5 group. The low-resolution mass spectrum cutoff at *m/e* 374 corresponds to the $H_{15}{}^{11}B_{10}{}^{12}C_5{}^{57}Co^{130}Te$ ion.

Table IV. 70.6-MHz Boron (^{11}B) NMR Data

Compd	Rel intens	Chem shifts, δ[a] (J_{BH}, Hz)
I[d]	1:2:2:2:1:2	−19.3 (149), 0.6 (164), ~2.1, 9.1 (156), 16.3 (151), 25.0 (154)
II[e]	3:4:1:1	0.1 (170), 2.6 (175), 9.7 (176), 36.3 (158)
III[d]	1:4:2:1:2	−21.4 (149), 3.2 (176), ~5.6, 14.0 (151), 24.8 (156)
IV[f]	2:2:1:4:1	6.0 (138), 9.5 (147), ~15, 16.8 (143),[c] 35.9 (139)
V[f]	2:3:2:2:1	5.4 (139), 12.4 (139),[c] ~16.9, ~18.3, 33.7 (147)
VI[f]	1:2:3:2:2	~−8.8 (~145), −6.3 (133), −0.9 (130),[c] 14.1 (135), ~17.3 (~167)
VII[f]	1:2:1:2:2:2	−12.4 (134), −5.7 (120), ~−3.4, ~1.5, 12.9 (137), 19.5 (142)
VIII[g]	1:3:2:2:2	−16.3 (149), −12.3 (132),[c] −6.1 (164), 7.0 (144), 10.7 (168)
IX[g]	1:1:2:2:2:2	−18.9 (144), −15.2 (143), −10.4 (135), −5.9 (157), 6.1 (144), 10.9 (152)
X[g]	1:2:1:2:2:2	−17.2 (145), −12.4 (140), −8.1 (150), −4.5 (170), 6.9 (144), 12.5 (161)
XI[g]	1:2:1:2:2:2	−19.9 (140), −13.7 (144), −9.1 (145), −4.2 (160), 6.2 (145), 13.6 (162)
$B_{10}H_{12}S$[h]	1:2:2:2:1:2	−16.4, 1.7, 4.5, 10.8, 17.7, 24.9

[a] Relative to $BF_3{\cdot}O(C_2H_5)_2 = 0$. [b] Broad resonance. [c] Unsymmetrical doublet. [d] Solvent chloroform. [e] Solvent methylene chloride. [f] Solvent acetonitrile. [g] Solvent acetone-d_6. [h] Solvent benzene.

Results and Discussion

The reaction of ammonium polysulfide with decaborane forms the $B_9H_{12}S^-$ ion in high yield.[1] However the similar reaction of ammonium polyselenide or polytelluride forms $B_{10}H_{11}Se^-$ and $B_{10}H_{11}Te^-$, respectively, in moderate to good yield. Protonation of these anions gives $B_{10}H_{12}Se$ and $B_{10}H_{12}Te$ in good yield. The 70.6-MHz ^{11}B NMR spectra of $B_{10}H_{12}S$ and $B_{10}H_{12}Se$ contain very similar doublet patterns. The spectrum of $B_{10}H_{12}Te$ also is similar but somewhat compressed (see Table IV). The most interesting feature of these spectra is the low-field doublet of area 1. The ^{11}B NMR spectra of all compounds of the general formula $B_{10}H_{12}E$ (E = S, Se, Te, As^-, $AsCH_3$, CH^- etc.) have this feature.[2] It is not certain whether this signal is due to the boron atom opposite the open face or that opposite the E group in the cage. Boron-11 spin–lattice relaxation measurements suggest that this doublet signal is due to the boron atom opposite the E group.[3] It may be that this effect is related to the antipodal effect found in icosahedral heteroatom borane systems[4] but further work needs to be done to prove this point.

The $N(CH_3)_4[B_{10}H_{11}E]$ salts were prepared in their purest form by deprotonation of the corresponding $B_{10}H_{12}E$ compound. Proton removal from the neutral derivative, isolation of the tetramethylammonium salt, and protonation to regenerate $B_{10}H_{12}Se$ was accomplished with overall recovery of 82% of the starting material. The ionic compounds are somewhat unstable and the surface of the solid darkens in air within a few days. The ^{11}B NMR spectra of the $B_{10}H_{11}E^-$ ions (E = S, Se, Te) are all very similar. The spectrum of the tellurium derivative displays the most detail with a 2:3:2:2:1 pattern of doublets. The area 3 doublet is not symmetrical suggesting the overlap of two resonances.

The novel compound $B_9H_9Se_2$ was obtained directly as a by-product in the polyselenide reaction with decaborane. The low-resolution mass spectrum cutoff at *m/e* 270 corresponds

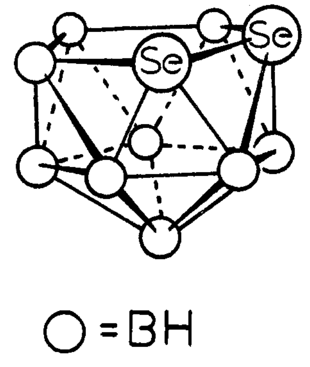

Figure 1. Proposed structure of $B_9H_9Se_2$.

to the $^{11}B_9H_9{}^{80}Se^{82}Se$ parent ion. The isotope ^{82}Se is present in only 9.19% natural abundance. The probability of having a parent ion with all ^{11}B and all ^{82}Se isotopes is very low. Even though the parent ion peak is relatively intense, the highest expected peak was not observed. The high-resolution mass spectrum contains a peak at *m/e* 269.9891 which corresponds to $^{11}B_9{}^1H_9{}^{80}Se^{82}Se$, having a calculated mass of 269.9874. The observed osmometer molecular weight of 266 is in fairly close agreement with the proposed molecular formulation. The 70.6-MHz ^{11}B NMR spectrum contains a 3:4:1:1: pattern of doublets which does not yield much structural information. We postulate that this molecule has an 11-atom nido cage structure as illustrated in Figure 1. The positions of the selenium atoms in the cage structure are uncertain based on the available data. A single-crystal x-ray structure determination of other molecules of this type (e.g., $B_8C_2H_{10}{}^{2-}$ or $B_{10}H_{10}S^{2-}$) has not been reported. An x-ray structure study of $B_9H_9Se_2$ is in progress.

Transition Metal Derivatives. Treatment of $B_{10}H_{12}Se$ or $B_{10}H_{12}Te$ with aqueous potassium hydroxide and $FeCl_2{\cdot}6H_2O$ forms purple $[N(CH_3)_4]_2Fe(B_{10}H_{10}Se)_2$ and green $[N(CH_3)_4]_2Fe(B_{10}H_{10}Te)_2$ in low yield. Attempted purification of the tellurium–iron derivative by column chromatography on silica gel without excluding air gave a yellow-green complex. The ^{11}B NMR spectrum of this product has signals which occur over a large chemical shift range similar to those of other known iron(III) paramagnetic compounds. Further characterization of this oxidized compound is in progress.

Under aqueous base conditions cobalt(III) chloride and $B_{10}H_{12}Se$ or $B_{10}H_{12}Te$ form orange $N(CH_3)_4[Co(B_{10}H_{10}E)_2]$ (E = Se or Te) in low yield. With anhydrous conditions $B_{10}H_{12}E$ (E = Se or Te) are deprotonated by triethylamine in the presence of cyclopentadiene monomer and cobalt(II) chloride to give the yellow compounds $(C_5H_5)Co(B_{10}H_{10}E)$ in moderate yields. The ^{11}B NMR spectra of icosahedral heteroatom boranes of the general type $(B_{10}H_{10}E)Co$(ligand) (where E = CH^-, As^-, P^-, PR, S, Se, or Te)[5] all have the expected 1:1:2:2:2:2 pattern of resonances. In most cases the area 1 doublets which are due to the boron atoms antipodal to the cobalt and E units are in the low-field part of the spectrum and vary in shielding the most. The ^{11}B NMR spectra of compounds VIII–XI fit well into this general spectral pattern. The 32-MHz ^{11}B NMR spectrum of $Co(B_{10}H_{10}S)_2{}^-$ reported previously,[1] although not well resolved, is consistent with the spectra obtained for the selenium and tellurium analogues.

All of these compounds have good to moderate thermal stability and chemical stability to moist air. Further synthetic studies in this area are in progress.

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Coordination of Organophosphorus Anions. 6.[1] Characterization of Nitrato Complexes of Cobalt(II), Nickel(II), and Zinc(II). Crystal and Molecular Structure of the Dimeric Nitrato(γ-piperidino β-ketophosphonate)cobalt(II)

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The γ-amino β-ketophosphonate ligand $(C_2H_5O)_2P(O)CH_2COCH_2R$ (R being the amino group $N(CH_3)_2$, $N(C_2H_5)_2$, $N(CH_2)_5$, or $N(CH_2)_4O$) forms dimeric molecular complexes with cobalt(II), nickel(II), and zinc(II) nitrates with the formula $(M(NO_3)L)_2$. The crystal and molecular structure of $(Co(NO_3)((C_2H_5O)_2P(O)CHCOCH_2N(CH_2)_5))_2$ is reported. The compound crystallizes in the monoclinic space group $P2_1/c$, with $a = 11.47$ (4) Å, $b = 12.83$ (2) Å, $c = 13.11$ (3) Å, $\beta = 113.15$ (10)°, $V = 1775$ (20) Å^3, and $Z = 2$. Observed and calculated densities are 1.47 (3) and 1.49 g cm^{-3}, respectively. Full-matrix least-squares refinement has converged with $R = 0.09$ for the 2282 reflections with $\sigma(I)/I < 1$. Each cobalt atom is six coordinated by an asymmetrically bidentate nitrato group and the terdentate OON organic moiety; the two octahedra sharing an edge are linked by means of the oxygen atoms of the carbonyl groups. Physical measurements indicate that similar structures are found for $(M(NO_3)L)_2$ ($M^{2+} = Co^{2+}$, Ni^{2+}, Zn^{2+}, and L^- with each amino group).

Introduction

In previous studies,[2-4] it was shown that the coordinating behavior of the γ-amino β-ketophosphonates $(C_2H_5O)_2P(O)CH_2COCH_2R$, designated by LH ($L_aH$, R = $N(CH_3)_2$; L_bH, R = $N(C_2H_5)_2$; L_cH, R = $\overline{NCH_2CH_2OCH_2CH_2}$; L_dH, R = $\overline{NCH_2CH_2CH_2CH_2CH_2}$) toward cobalt, nickel, and zinc ions is well demonstrated by the formation of halogeno or

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