On the basis of the monoclinic choice, two possibilities still exist. The longest real axis was arbitrarily chosen as the unique one. Nonextinction conditions $h + k = 2n$ indicated C centering. The possible monoclinic space groups are C2 (no. 5), Cm (no. 8), and C2/m (no. 12). From measurements of the displacement of reciprocal lattice levels relative to the $l = 0$ level, β was established as $90 \pm 1.5°$. If the axis of intermediate length is proved to be the unique one in monoclinic symmetry, the space group will be P2 (no. 3), Pm (no. 6), or P2/m (no. 10).

Several Debye–Scherrer powder patterns were obtained for the several preparations. The pattern which was characterized as arising from the most nearly pure B_2S_3 sample was obtained with Cu Kα radiation (λ 1.5418 Å, Ni filter, 114.6-mm diameter camera) from crushed crystals of a fourth preparation. The relative intensities and d spacings were similar to those obtained by Hagenmuller and Chopin. Lines in the back-reflection region were disperse, very weak, or absent. Indexing was accomplished on the basis of the pseudoorthorhombic cell indicated by the Weissenberg single-crystal data. Table I contains the indexing, observed intensities, and observed and calculated d values for B_2S_3 from film C 4075. All observed lines were indexed. A comparison between the intensities from the powder pattern and from the single-crystal films showed excellent agreement. In particular, the fact that the most intense reflections observed by single-crystal methods were also the most intense reflections observed in the powder pattern gave strong evidence that the powder pattern was indexed correctly.

TABLE I

POWDER DIFFRACTION PATTERN OF MONOCLINIC (PSEUDOORTHORHOMBIC) B_2S_3[a]

h	k	l	I_{obsd}	d_{obsd}, Å	d_{calcd}, Å
0	4	1	5	7.00	7.016
0	6	1	10	5.35	5.356
0	8	0	1	4.65	4.636
0	8	1	1	4.26	4.256
1	1	0	5	4.02	4.024
1	1	1	10	3.77	3.768
1	3	1	1	3.62	3.621
1	5	0	100	3.55	3.553
0	10	2	7	3.05	3.051
1	5	2	5	2.97	2.962
1	7	2	20	2.76	2.759
0	0	4	50	2.68	2.682
0	12	2		2.68	2.678
0	2	4	5	2.66	2.655
1	9	2	5	2.55	2.543
1	5	3	5	2.52	2.521
1	11	1		2.52	2.518
0	14	2	5	2.37	2.375
1	13	1	1	2.28	2.279
1	9	3	1	2.25	2.247
1	3	4	1	2.20	2.200
1	5	4	5	2.14	2.141
2	6	1	5	1.89	1.893
1	17	1		1.89	1.890
1	17	2	5	1.81	1.808

[a] $a_0 = 4.048 \pm 4$, $b_0 = 37.09 \pm 4$, $c_0 = 10.73 \pm 1$ Å; $\alpha = \beta = \gamma = 90°$.

Lattice parameters were obtained from a least-squares treatment[3] of 23 Debye–Scherrer maxima.

The crystal data are: diffraction symbol, 2/m; crystal system, C-centered monoclinic; space group, C2, Cm, or C2/m; lattice parameters, $a_0 = 4.048 \pm 0.004$ Å, $b_0 = 37.09 \pm 0.04$ Å, $c_0 = 10.73 \pm 0.01$ Å, $\beta = 90 \pm 1.5°$. The cell content Z is calculated to be 14.1 ± 0.4 based on an estimated error in the density of 0.05 g/cm^3.

Attempts to index the powder patterns of the selenium analog B_2Se_3 given by Hutchinson and Eick[4] and by Cueilleron and Hillel[5] which are drastically different from each other have not been successful.

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Syntheses of Nonahydrononaborate(2−) Salts

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The preparation and characterization of salts containing the $B_9H_9^{2-}$ anion were first reported by Klanberg and Muetterties.(1) These workers found that pyrolysis of alkali metal salts of the $B_3H_8^-$ anion under vacuum at 200–230° resulted in the formation of salts of BH_4^-, $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$, and $B_9H_9^{2-}$. The anion was characterized by its ultraviolet, infrared, and boron-11 nmr spectra. Its structure has been established to be a tricapped trigonal prism by Guggenberger.(2)

We wish to report two new methods of synthesizing salts of the $B_9H_9^{2-}$ anion. The first method involves the pyrolysis of salts containing the $B_{10}H_{12}^{2-}$ anion.(3) Decomposition of $Na_2B_{10}H_{12}$ is complete at temperatures above 230–240° and the product contains $B_9H_9^{2-}$ as well as $B_{10}H_{10}^{2-}$ salts. The $B_9H_9^{2-}$ anion was recovered from the reaction mixture by solution in water, precipitation as the rubidium or cesium salt, and fractional recrystallization of the initial product. It can also be precipitated as the thallium(I) salt which is

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almost totally insoluble in water at room temperature. This does not serve to separate $B_9H_9^{2-}$ from $B_{10}H_{20}^{2-}$ which also forms an insoluble Tl(I) salt. $Cs_2B_9H_9$ was also prepared in a similar fashion from the mixture obtained from the pyrolysis of $K_2B_{10}H_{12}$ to 300°.

The second method for preparing $B_9H_9^{2-}$ salts involves the pyrolysis of the $B_{10}H_{14}^{2-}$ salts. The pyrolysis of $Na_2B_{10}H_{14}$ was reported by Toeniskoetter[4] to produce slightly more than four atoms of hydrogen per formula weight of $B_{10}H_{14}^{2-}$ at temperatures between 120 and 190°. He observed that the product thus obtained corresponded closely to the formula $Na_2B_{10}H_{10}$ and did not give up any more hydrogen until a temperature of 350° was reached, but he did not pursue the matter further. We found that $Rb_2B_{10}H_{14} \cdot nH_2O$ may be pyrolyzed to yield a mixture of $Rb_2B_9H_9$ and $Rb_2B_{10}H_{10}$. The mixture was separated by fractional crystallization.

The salts were characterized by comparison of their ^{11}B nmr and infrared spectra and X-ray powder diffraction patterns with those of authentic samples prepared by the method of Klanberg and Muetterties[1,5] and, in the case of $Cs_2B_9H_9$, a sample provided by those authors. The ^{11}B nmr spectrum of $Rb_2B_9H_9$ in aqueous solution consists of a high-field doublet centered at +40.0 ppm and a low-field doublet centered at +21.9 ppm relative to $B(OCH_3)_3$ as an external reference. This is in excellent agreement with the values reported by Klanberg and Muetterties. In dimethyl sulfoxide the high-field doublet appears at 38.6 ppm, the low-field doublet appears at 21.0 ppm, and the B–H coupling constants are 120 and 135 cps, respectively. The area of the high-field doublet is approximately twice that of the low-field doublet and the peaks appear to be very symmetrical. $Rb_2B_9H_9$ after being heated in a quartz tube *in vacuo* to a temperature of 400° and held at this temperature for 15 min is recovered unchanged. If heating is continued at the rate of 10°/min, only insignificant amounts of hydrogen are evolved under 500°.

It appears likely that the thermal degradation of the $B_{10}H_{14}^{2-}$ ions proceeds through the $B_{10}H_{12}^{2-}$ ion. It was not found feasible to stop the pyrolysis at this intermediate step and no direct evidence was obtained for the presence of this intermediate.

Experimental Section

Pyrolysis of $B_{10}H_{12}^{2-}$ Salts.—$Na_2B_{10}H_{12}$ was prepared in tetrahydrofuran by the method of Wilks and Carter.[3] In a typical reaction 0.326 g of $Na_2B_{10}H_{12}$ containing about 5% tetrahydrofuran (1.9 mmol) was crushed in a mortar and pestle in a drybox, placed in a 12-in. reaction tube, and attached to a vacuum line. After evacuating, a stirred oil bath was placed around the reaction tube, the temperature was raised at a rate of 150–250°/hr, and hydrogen evolution was followed using a Toepler system. After the temperature reached 240°, no further hydrogen was evolved over a 10-min period. The total hydrogen evolved was 2.01 mmol. The only condensable materials obtained on pyrolysis were shown to be tetrahydrofuran by the infrared spectrum of the gas.

$Rb_2B_9H_9$.—The $Na_2B_{10}H_{12}$ prepared from 1.21 g of sodium hydride (50.4 mmol) and 3.08 g of decaborane(14) (25.2 mmol) was pyrolyzed over a 2-hr period. On cooling, the product was dissolved in 100 ml of absolute ethanol. A solution containing 6.5 g of RbCl (54 mmol) dissolved in 70 ml of 50:50 ethanol–water was added slowly to the reaction mixture. The mixture was cooled in a freezer for 1 hr and filtered through a glass frit. The crude solid was washed with absolute ethanol and anhydrous ethyl ether and was then dissolved in 60 ml of water made slightly alkaline with rubidium carbonate at a temperature of 50° under a nitrogen stream. The solution was filtered, the volume was doubled with absolute ethanol, and the mixture was placed in a freezer for 30 min. The precipitate was filtered and washed with absolute alcohol and ethyl ether; 2 g of material was obtained that was essentially pure $Rb_2B_9H_9$. A second recrystallization with 20 ml of water at 50° and 20 ml of absolute ethanol produced 1.0 g (3.5 mmol) of pure $Rb_2B_9H_9$. The major product was $Rb_2B_{10}H_{10}$ which was recovered and identified by its ^{11}B nmr and infrared spectra. Observed X-ray powder data (*d*, Å) are: 4.21 (vs), 3.83 (mw), 3.53 (m), 3.27 (w), 3.16 (ms), 2.76 (m), 2.54 (m), 2.43 (ms), 2.30 (vw), 2.23 (mw), 2.08 (vw), 1.97 (ms), 1.93 (w), 1.89 (vw), 1.85 (w), 1.78 (vvw), 1.76 (vvw), 1.74 (vvw), 1.68 (w), 1.64 (mw), 1.60 (w), 1.59 (vw), 1.54 (w), 1.48 (vvw), 1.46 (vw), 1.42 (vw), 1.37 (vvw).

$Cs_2B_9H_9$.—A 4.65-g sample of pyrolysis product from 28.3 mmol of $Na_2B_{10}H_{12}$ was dissolved in 50 ml of absolute alcohol. Cesium bromide (13.0 g, 61 mol) dissolved in 350 ml of 85% ethanol were added to the solution. The reaction mixture was allowed to digest for 15 min and then passed through a large fritted funnel. The residue was washed with two 30-ml portions of absolute ethanol and dissolved in 550 ml of water at 37°. To this solution was added 150 ml of 95% ethanol, and the cloudy mixture was placed in a freezer overnight and then thawed to the consistency of a thick slush and passed through a filtering funnel. The residue was washed with 20 ml of ethanol and dried in a vacuum line. This produced 4.0 g of crude $Cs_2B_9H_9$. The crude product was dissolved in 350 ml of water at 37°, mixed with 150 ml of 95% ethanol, and again placed in the freezer. A 2.6-g yield of product was obtained on this recrystallization which was recrystallized a third time in 250 ml of water and 100 ml of 95% ethanol. The third recrystallization produced 1 g (2.7 mmol) of pure $Cs_2B_9H_9$. Observed X-ray powder data (*d*, Å) are: 4.40 (m), 4.30 (s), 4.02 (m), 3.65 (m), 3.42 (vw), 3.23 (m), 2.84 (w, br), 2.62 (m), 2.52 (s), 2.42 (vw), 2.36 (vvw), 2.29 (w), 2.13 (vw), 2.02 (mw), 1.94 (w), 1.69 (w), 1.66 (vw), 1.61 (vw), 1.51 (vvw), 1.45 (vvw).

$Tl_2B_9H_9$.—Mixture of approximately equimolar amounts of aqueous solutions of $Rb_2B_9H_9$ and Tl_2SO_4 resulted in the precipitation of $Tl_2B_9H_9$ which was removed by filtration. The salt is yellow and was identified by its ^{11}B nmr spectrum in dimethyl sulfoxide. (*Caution*! The ability of dimethyl sulfoxide to be absorbed through the skin, the high toxicity of thallium compounds, and the unknown toxic effects of the borane anion make the solutions potentially hazardous.) Observed X-ray powder data (*d*, Å) are: 5.30 (m), 4.15 (vs), 3.75 (m), 3.49 (m), 3.23 (mw), 3.13 (ms), 2.74 (ms), 2.52 (m), 3.40 (ms), 2.26 (w), 2.22 (w), 2.06 (w), 1.96 (m), 1.91 (vw), 1.88 (vw), 1.83 (w), 1.76 (vvw), 1.73 (vvw), 1.67 (vw), 1.63 (mw), 1.58 (vw), 1.56 (vw), 1.52 (w), 1.47 (vvw), 1.40 (vvw), 1.37 (vvw).

$Rb_2B_9H_9$ from $Rb_2B_{10}H_{14} \cdot nH_2O$.—The hydrate of $Rb_2B_{10}H_{14}$ was prepared by the method of Muetterties.[6] It was recrystallized from water at 60°. Higher temperature produced the salt with considerable contamination by hydrolysis products. A 10.8-g sample of $Rb_2B_{10}H_{14} \cdot nH_2O$ was pyrolyzed in a vacuum line in a large reaction tube to a temperature of 310°. Most of the hydrogen was evolved between 225 and 250°. The residue was dissolved in 80 ml of water containing 2 mg of rubidium carbonate at 55°. Thirty milliliters of warm 95% ethanol was added. The mixture was rewarmed to dissolve the flocculent material which had precipitated on addition of the alcohol, then placed in the freezer for 30 min, filtered, and washed with absolute ethanol and ethyl ether. A 1.2-g yield of material was obtained. This was dissolved in 22 ml of water at 36° and a pH of

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8–9. Five milliliters of absolute alcohol was added, the solution was placed in a freezer for 90 min, and 0.96 g (3.3 mmol) of pure $Rb_2B_9H_9$ was collected upon filtering.

The ^{11}B nmr spectra were obtained on Varian spectrometers operating at frequencies of 19.2 and 32.1 MHz. Chemical shift data are given relative to trimethoxyborane as an external standard.

Debye–Scherrer–Hull X-ray powder diffraction patterns were taken by Mr. C. Scherone of Westinghouse Electric Corp. using a 114.6-mm camera.

Acknowledgment.—We wish to thank Dr. E. L. Muetterties for providing an authentic sample of $Cs_2B_9H_9$ and for his valuable comments which allowed us to characterize these materials correctly. We gratefully acknowledge support of this research by the National Science Foundation (Grant GP-8321) and by the Pennsylvania Science and Engineering Foundation (Contract 60).

Correspondence

On the Electron Spin Resonance Spectra of Oxovanadium(IV) Dithiocarbamate Complexes[1]

Sir:

Recently we have reported on the synthesis, structure, and infrared and optical spectra of N,N-dialkyldithiocarbamate (R = CH_3, C_2H_5, i-C_3H_7, and $CH_2(CH_2)_2CH_2$) complexes of oxovanadium(IV).[2] The only prior work on these complexes was by Garif'yanov and Kozyrev,[3] who reported the results of an esr study on the ethyl-substituted compound which was prepared and studied in solution without isolation and characterization as a solid. Subsequent to our publication was a report[4] by Selbin and Vigee on five VO^{2+}–dtc complexes, only one of which (the ethyl compound) overlapped our series. Three of the compounds prepared by Selbin and Vigee were formulated with a water molecule, whereas our compounds were anhydrous; aside from this difference the complexes reported in the two studies appear to be much the same.

Of particular interest is the behavior of the complexes in solution, since large red shifts are observed for certain of the optical bands in coordinating solvents. We interpreted the red shifts in terms of the addition of a solvent molecule to the coordination position *trans* to the oxygen atom, and very recently we have reported on our success in preparing as stable solids adducts of the methyl and pyrrolidine complexes with pyridine and 4-methylpyridine.[5] Thus the conclusion that dithiocarbamate complexes of oxovanadium(IV) are completely destroyed by pyridine and DMSO, as reached by Selbin and Vigee from their esr study in DMSO, was of considerable consequence and has stimulated us to investigate the esr spectral properties of the compounds that we reported previously, as well as to reinvestigate the cyclohexyl compound reported by Selbin and Vigee.

Compounds were prepared as reported previously,[2] and esr spectra were recorded at room temperature with a Varian Model E-3 spectrometer. The reference material used was DPPH in benzene. The isotropic hyperfine splittings were measured[6] as the separation between lines 4 and 5, and the accuracy of our techniques was estimated by measuring the spectral properties of $VO(acac)_2$ and $VOSO_4$. A comparison of our results to those previously reported indicates an agreement of ±1 G for the hyperfine splittings, as shown in Table I.

TABLE I

ISOTROPIC HYPERFINE SPLITTING CONSTANTS

Compound[a]	Solvent	$\Delta H_{4,5}$[b]	Ref[c]
$VO((c\text{-}C_6H_{11})_2dtc)_2$	CH_2Cl_2	86	
	Pyridine	88	
	DMSO	85	
	DMSO	114	*d*
$VO((CH_3)_2dtc)_2$	CH_2Cl_2	89	
	Pyridine	89	
	DMSO	93	
$VO((C_2H_5)_2dtc)_2$	CH_2Cl_2	89	
	Pyridine	89	
	DMSO	91	
	Benzene	92	*e*
$VO((i\text{-}C_3H_7)_2dtc)_2$	CH_2Cl_2	88	
	Pyridine	88	
	DMSO	87	
$VO((py)_2dtc)_2$	CH_2Cl_2	88	
	Pyridine	88	
	DMSO	93	
$VO(CH_3\text{-}c\text{-}C_6H_{11}dtc)_2$	DMSO	118	*d*
$VO(acac)_2$	Pyridine	105	
	Pyridine	104	*f*
$VO(acac)_2$	Benzene	109	
	Benzene	108	*g*
$VOSO_4$	H_2O	115	
	H_2O	116	*h*
$VOSO_4$	DMSO	112	
	DMSO	113	*i*

[a] dtc = dithiocarbamate; py = pyrrolidyl; acac = acetylacetonate. [b] Values in gauss. [c] Where a reference is not given, values were obtained in this work. [d] Reference 4. [e] Reference 3. [f] F. A. Walker, R. L. Carlin, and P. H. Rieger, *J. Chem. Phys.*, **45**, 4181 (1966). [g] I. Bernal and P. H. Rieger, *Inorg. Chem.*, **2**, 256 (1963). [h] H. A. Kuska and M. T. Rogers in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience Publishers, New York, N. Y., 1968, Chapter 13. [i] Reference 6.

Throughout the preparations and spectral measurements, great care was taken to protect the dithiocarbamate samples from oxygen. Since it does appear[5] that the complexes *slowly* decompose in DMSO, the

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(1) This work was supported by the National Science Foundation through Grant No. GP-10668.

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