cm^{-1}) of the halide complexes described in the Experimental Section are (values in cm^{-1}): chloride: 304 s, 319 s, 476 m, 496 m, 1248 s, 1269 s; bromide: 461 m, 482 m, 1246 s, 1261 s; iodide, sample 1: 429 m, 449 m, 1225 s, 1241 s, 1252 s, 1279 s; iodide, sample 2: 430 m, 451 m, 1227 s, 1241 s, 1252 s, 1281 s.

The values for the chloride and bromide agree very closely with those reported earlier for the *cis* complexes and there seems little doubt that the present samples also have the *cis* configuration. The spectrum of the iodide is similar to what might be expected for *cis*-$Pd(NH_3)_2I_2$. It shows a doublet in the ν(Pd–N) region which continues the trend of decreasing frequencies from Cl to I, a trend that is also apparent in the three *trans* complexes.[7] It also shows several strong peaks in the 1200–1300-cm^{-1} region rather than the single strong peak with a shoulder that seems to characterize the *trans* isomers. However, there are four of these strong peaks rather than the two found in the *cis* chloride and bromide. The presence of additional peaks in the spectrum of the *cis* iodide could be due to its crystal structure being different from those of the *cis* chloride and bromide. Additional peaks could also arise from the presence of impurities such as $[Pd(NH_3)_4][PdI_4]$ and *trans*-$Pd(NH_3)_2I_2$ which show absorptions at 1278 and 1252 cm^{-1}, respectively.

The samples of chloride and bromide complexes showed considerable stability compared with those prepared by earlier methods. In both cases the doubling of the infrared peaks was still strongly evident when the measurements were repeated after 14 months, showing that isomerization had not occurred to any great extent. In the case of the iodide, however, samples showed some evidence of change after 1 month and, after 14 months, exhibited the spectrum of the *trans* isomer. These results tend to confirm the view of Durig and Mitchell[6] that the instability of these *cis* complexes results from the presence of impurities that catalyze the isomerization. Such impurities are less likely to contaminate the product when it is formed rapidly, as in the present experiments, than when it is formed slowly, as in the method used by Grinberg and Shulman. The iodide is probably inherently the least stable of the three *cis* halo complexes and is also probably the least pure of the present samples. The attempt to prepare *cis*-$Pd(NH_3)_2(SCN)_2$ by the present technique resulted in the formation of a pink compound. The ionic dimers $[Pd(NH_3)_4][PdX_4]$ are generally pink and this product was almost certainly the known compound $[Pd(NH_3)_4][Pd(SCN)_4]$. It is interesting that difficulties in preparing *cis*-diacidodiamminepalladium(II) complexes are encountered with several ligands (such as I^-, SCN^-, NO_2^-) that occur high in the *trans*-effect series for Pt(II). The formation of predominantly *cis*-$Pd(NH_3)_2(H_2O)_2^{2+}$ in the aquation of $Pd(NH_3)_4^{2+}$ is also consistent with the Pt(II) *trans*-effect order, $NH_3 > H_2O$.

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High Molecular Weight Boron Sulfides. VI. The Unit Cell of Monoclinic Diboron Trisulfide[1]

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The purpose of this paper is to describe the unit cell of B_2S_3 as obtained from single-crystal Weissenberg and Debye–Scherrer powder X-ray diffraction patterns. Although B_2S_3 has been known for more than a century, crystalline samples were first reported in 1962 by Hagenmuller and Chopin,[2] who prepared them by decomposition of $(HBS_2)_3$ at 100°. These authors apparently could not, however, index the complicated powder pattern. The present authors have used several techniques to prepare B_2S_3 in order to perform a vaporization study of the boron–sulfur system. One of these techniques, as described below, yielded single crystals which were used for the crystallographic investigation.

A powdered mixture of FeS and boron was heated at 700–730° under a steady flow of dried helium in a graphite tube contained in a Vycor tube. White crystals of an average size of $0.1 \times 0.1 \times 0.2$ mm^3 were collected from the cool zones of the graphite tube for several separate preparations.

The limited amount of material collected from separate preparations prevented the complete characterization of each sample: chemical analysis, density, powder diffraction, single-crystal diffraction work, and vaporization studies were not performed on one sample concomitantly, yet the separate results appeared to be consistent.

The melting point was 563 ± 3°. Density measurements gave 1.71 and 1.72 g/cm^3 for a sample having a powder pattern very similar to the pattern listed below.

Chemical analysis of a sample prepared under vacuum slightly contaminated with graphite gave an S:B atomic ratio of 1.506 ± 0.005 with 99.1% recovery.

Single-crystal work was performed on crystals from a third sample. Approximate unit cell parameters and the symmetry properties for B_2S_3 were obtained from two different single crystals by Weissenberg photographs around the two shorter axes. No mirror in the diffraction effects was observed perpendicular to the shortest real axis. Perpendicular to both other axes approximate mirrors appeared to exist, but because the imperfections in the crystals gave rise to streaking and diffuseness of some diffraction spots, a resolution of this contradictory observation could not be made; *i.e.*, whether only one mirror (monoclinic case) or none at all (triclinic case) exists could not be firmly established.

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[1] Abstracted in part from the Ph.D. thesis of H. Y. Chen, submitted to the University of Kansas, 1969.

[2] P. Hagenmuller and F. Chopin, *C. R. Acad. Sci.*, **255** 2259 (1962).

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 $K\alpha$ 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/cm³.

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 $B_8H_8^-$ 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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