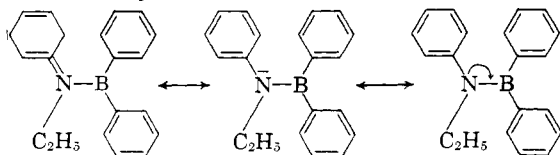


However, the phenyl substituents on the boron seem to have a lessened attraction for the pair, as indicated by the structures



The B-N double bond character of I, therefore, is somewhat stronger than in (ethylphenylamino)-diethylborane (II), where the boron-attached alkyl groups do not produce such a degree of electron delocalization on the B-N bond. Further weakening of the double bond character appears in dichloro-(diphenylamino)-borane (III), though the difference between II and III is not as great as expected. Presumably the N-attached phenyl rings in the latter case are not both coplanar with the rest of the molecule,<sup>6</sup> otherwise two of the *o*-hydrogens of the phenyl groups would constitute steric hindrance. The planarity is likely to be distorted thus affording a decrease of resonance which demonstrates why the second phenyl group on the nitrogen does not produce as much weakening of the B-N double bond character as one might expect.

TABLE III  
INFRARED ABSORPTION OF THE B-N BOND OF SOME AMINO-BORANES

Compound	Absorption, cm. <sup>-1</sup>
(Monophenylamino)-dimethylborane <sup>6</sup>	1330
Dimethyl-(pyrrolo)-borane <sup>6</sup>	1343
(Methylnaphthylamino)-dimethylborane	1370
Dichloro-(diphenylamino)-borane <sup>6</sup>	1378
(Ethylphenylamino)-diethylborane	1408
(Ethylphenylamino)-diphenylborane	1424
(Di- <i>sec</i> -butylamino)-diethylborane	1459
Dichloro-(diethylamino)-borane <sup>1</sup>	1505
(Amino)-dimethylborane <sup>8</sup>	1515
Dichloro-(dimethylamino)-borane <sup>9</sup>	1526
(Dimethylamino)-dimethylborane <sup>8</sup>	1530

The influence of substituents on the stability and bond characteristics of the B-N linkage of aminoboranes is under further investigation; the findings will be published later.

Acknowledgment is accorded to the Schwarzkopf Microanalytical Laboratory, Woodside 77, New York, for analyses reported herein.

(8) H. J. Becher and J. Goubeau, *Z. anorg. allgem. Chem.*, **268**, 133 (1952).

(9) J. Goubeau, M. Rahtz and H. J. Becher, *ibid.*, **275**, 161 (1954).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

## Infrared and Visible Spectra of Gaseous B<sub>2</sub>S<sub>3</sub> at High Temperatures<sup>1</sup>

BY FRANK T. GREENE AND JOHN L. MARGRAVE

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Infrared emission and absorption spectra of gaseous B<sub>2</sub>S<sub>3</sub> have been observed for the normal isotopic mixture and for a sample prepared with B<sup>10</sup>. Examination of the isotope shifts with the aid of the Redlich-Teller product rule gives support to a twisted zigzag model for B<sub>2</sub>S<sub>3</sub> with C<sub>2</sub> symmetry. Electronic absorption spectra were observed in the regions 5400-7200 Å., 3900-4200 Å., and 3100-3500 Å.

During the past few years considerable attention has been given to the determination of the fundamental properties of B<sub>2</sub>O<sub>3</sub>.<sup>2</sup> Its sulfur analog, B<sub>2</sub>S<sub>3</sub>, has, however, been neglected almost entirely.

**Infrared Studies of Gaseous B<sub>2</sub>S<sub>3</sub>.**—An infrared spectroscopic investigation of gaseous B<sub>2</sub>S<sub>3</sub> has been made over the range 600-1000°. For this work, B<sub>2</sub>S<sub>3</sub> was prepared by passing dried H<sub>2</sub>S through amorphous boron at 700° and collecting the vaporized product on a cold finger. The resulting product contains HBS<sub>2</sub>, B<sub>2</sub>S<sub>3</sub> and some sulfur and boric acid impurity. Single crystals, apparently of HBS<sub>2</sub>, have been prepared and are being studied. This mixture was introduced directly into a 1-inch quartz or Vycor tube to which suitable windows were attached and heated *in vacuo* at 300 and 600° for several hours until degassed and all H<sub>2</sub>S removed. At the higher temperatures there was considerable condensation of vaporized material as a white smoke in cool portions of the tube and usually about 100 mm. of dry argon was introduced to prevent boiling and retard diffusion just before the temperature was raised to that of a run.

(1) Presented before the 135th Meeting, American Chemical Society, Boston, April, 1959.

(2) (a) D. A. Dows and R. F. Porter, *THIS JOURNAL*, **78**, 5165 (1956); (b) D. White, P. N. Walsh and D. E. Mann, *J. Chem. Phys.*, **28**, 508 (1958); (c) E. N. Lotkova, V. V. Obukhov-Denisov, N. N. Sobolev and V. P. Cheremichinov, *Optics and Spectroscopy (Russian)*, **1**, 772 (1956); **3**, 560 (1957); (d) W. Taylor, *J. Chem. Phys.*, **28**, 625 (1958).

The spectrum of the gas over B<sub>2</sub>S<sub>3</sub> was examined in emission and absorption in the region 10,000 to 400 cm.<sup>-1</sup> with a Beckman Model IR 2 spectrometer. The source housing was separated about 1 meter from the entrance optics and a 12-inch nichrome furnace containing a quartz or Vycor tube with KBr windows was inserted. For emission studies with this instrument, an external chopper which could be synchronized with the synchronous rectifier was mounted in front of the entrance optics. For the longer wave length region, a Perkin-Elmer Model 112 double pass spectrometer with a CsBr prism was used in emission out to 300 cm.<sup>-1</sup>. For emission work, a series of diaphragms was used to mask out wall radiation. Several tracings were made for each spectral region studied at a variety of temperatures and with a number of different samples.

Five bands were observed both in emission and absorption. Their maxima were at 1322, 990, 919, 859 and 602 cm.<sup>-1</sup>. When boron containing 95% B<sup>10</sup> was substituted for the normal isotopic mixture, the bands were observed to shift to 1389, 1040, 952, 906 and 605 cm.<sup>-1</sup>. This isotope shift is probably too small as a result of the overlapping of B<sup>10</sup>-B<sup>11</sup> bands with B<sup>11</sup>-B<sup>11</sup> bands; correction for this effect indicates net isotope shifts of 71, 54, 37, 51 and 6 cm.<sup>-1</sup>, respectively.

There are several chemically plausible models for B<sub>2</sub>S<sub>3</sub>: a linear molecule (D<sub>∞h</sub>), a bipyramid (D<sub>3h</sub>), a plane V or W-shaped molecule (C<sub>2v</sub>) or a twisted zigzag (C<sub>2</sub>). An upper limit for the isotope shift permitted for a given model can be calculated

from the Redlich-Teller product rule<sup>3</sup> since this rule gives the product of the ratios of the frequencies of the isotopically substituted molecules for each vibrational frequency and since the frequency must remain the same or increase on substitution of a lighter isotope.

The observed frequency ratios for the isotopic molecules are

$$1389/1318 = 1.053 \quad 1040/986 = 1.056 \quad 952/915 = 1.040 \\ 906/855 = 1.060 \quad 605/599 = 1.010$$

If the frequencies observed are fundamentals of  $B_2S_3$ , then it can be shown that the  $D_{3h}$  and  $D_{\infty h}$  structures are inconsistent with the observed shifts. The  $C_{2v}$  point group is not eliminated directly by the product rule. However, the most plausible assignment of the observed frequencies seems to favor the  $C_2$  structure as the only chemically sound structure which is consistent with the observed isotope shifts. Other models, which

(3) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945.

require violation of classical valences, have been tentatively rejected.

If the  $C_2$  model is correct, there should be nine infrared active fundamentals of which only five have been observed. The remaining four frequencies almost certainly belong to weaker bending modes and might be below the limit of detectability.

**Visible and Ultraviolet Spectra of  $B_2S_3$ .**—The electronic spectrum of the gas over  $B_2S_3$  at  $1000^\circ$  was investigated in absorption from 3000 to 7400 Å. with a Bausch and Lomb 1.5 meter grating. A No. 2 photoflood and a xenon arc were used as light sources. Bands were observed in the regions 5400–7200, 3900–4200 and 3100–3500 Å. The red band system bears at least a superficial resemblance to the green system of  $B_2O_3$ .

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

## Thallium-Tungsten Bronze: A Solid State Defect Structure<sup>1</sup>

BY M. J. SIENKO

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Thallium-tungsten bronzes,  $Tl_xWO_3$ , have been prepared ranging in composition from  $x = 0.19$  to  $x = 0.36$ . Preparation methods included: (1) heating  $Tl_2WO_4$ ,  $WO_3$  and W; (2) vapor phase reaction of Tl and  $WO_3$ ; (3) electrolysis of  $Tl_2CO_3$  and  $WO_3$  mixtures. Products were crystalline and powder diagrams could be indexed in the tetragonal system with  $a = 7.31$  Å. and  $c = 12.80$  Å. Electrical resistance measurements using a potential probe method on single crystals indicated metallic conduction with specific resistivity varying from  $6.0 \times 10^{-3}$  ohm-cm. at  $25^\circ$  to  $9.0 \times 10^{-3}$  ohm-cm. at  $240^\circ$ . Thermoelectric power at room temperature was  $-20$  microvolts per degree referred to platinum, suggesting one free electron per thallium atom. A general model is proposed for the tungsten bronzes  $M_xWO_3$  where M is viewed as giving rise to local energy levels in the forbidden gap between the conduction and valence bands of  $WO_3$ .

The tungsten bronzes,<sup>2</sup>  $M_xWO_3$ , in which M is a univalent metal and  $x$  lies between 0 and 1, represent an unusually interesting series of non-stoichiometric materials with properties ranging from metallic to semi-conducting depending on what M is. If M is sodium, the resulting sodium-tungsten bronze shows a linear increase of resistance with temperature and a Hall coefficient corresponding to one free electron per sodium atom<sup>3</sup>; if M is copper or silver, the resulting tungsten bronze shows an exponential decrease of resistance with rising temperature.<sup>4</sup> In both cases, magnetic susceptibility is low and independent of temperature. In attempting to set up a general model to account for these observations, we have been led to reject the older view of  $M_xWO_3$  as a solid solution of  $WO_3$  in hypothetical  $MWO_3$  in favor of a model in which  $M_xWO_3$  is viewed as a solid solu-

tion of M in  $WO_3$ . In this view  $M_xWO_3$  is considered to be a solid state defect structure in which holes in a  $WO_3$  network (conceivably greatly distorted from pure  $WO_3$ ) are randomly occupied by M atoms with the M atoms more or less dissociated into  $M^+$  ions and free electrons. The electrical and magnetic properties would then be explainable as functions of the tightness of binding of the electrons to the atoms M and to the host lattice. The striking chemical inertness invariably observed for metal-tungsten bronzes could be explained in terms of a "caging effect" of the  $WO_3$  lattice on the ions  $M^+$ —only a negligible number of electrons could be removed from a metal-tungsten bronze crystal without building up an enormous space charge.

As part of a general program to determine necessary conditions for change-over from metallic to semi-conducting properties, we have tried to insert various metal atoms into the  $WO_3$  lattice. It turns out to be extraordinarily difficult to achieve this with anything but the alkali metals and the copper subgroup metals. However, we have now succeeded in getting thallium in  $WO_3$ , and it is the preparation and properties of such a "thallium-tungsten bronze,"  $Tl_xWO_3$ , that are described in this paper. The implications of these properties

(1) This research was supported in whole or in part by the United States Air Force under Contract No. AF 49(638)-191 monitored by the AF Office of Scientific Research of the Air Research and Development Command.

(2) See, for example, G. Hägg, *Z. physik. Chem.*, **B29**, 192 (1935); M. E. Straumanis and S. S. Hsu, *This Journal*, **72**, 4027 (1950); A. Magnéli and B. Blomberg, *Acta Chem. Scand.*, **5**, 377 (1951); L. E. Conroy and M. J. Sienko, *This Journal*, **74**, 3520 (1952).

(3) E. J. Huibregtse, D. B. Barker and G. C. Danielson, *Phys. Rev.*, **84**, 142 (1951)

(4) L. E. Conroy and M. J. Sienko, *This Journal*, **79**, 4048 (1957).