Interstitial Compounds of Boron

BY V. I. MATKOVICH*

A model of the structure of boron compounds is presented which explains such compounds as $B_{13}O_2$, B_4C, $B_{13}C_2$, $B_{13}P_2$, $B_{13}As_2$ and B_4Si as a group of interstitial compounds of boron. Formation of a new boron sulfide, $B_{12}S$, belonging to the same group is reported.

Introduction

Recent developments indicate that such compounds as B_4Si^{1-3} and $B_{13}P_2^4$ as well as both boron carbides B_4C and $B_{13}C_2^{5,6}$ can be derived from a recently discovered boron modification[7,8] by placing the corresponding elements in its interstitial openings. A study of the boron–sulfur system has been carried out as a part of investigation of compounds related to boron or boron carbides.

Mechanism of Formation of Interstitial Boron Compounds.—According to Zhdanov and Sevastyanov[9] and Clark and Hoard[10] the B_4C structure consists of linar chains of three carbon atoms and groups of twelve boron atoms placed at the vertices of nearly regular icosahedra. These are distributed in a rhombohedron in a NaCl type arrangement. The smallest rhombohedron representing the unit cell contains three B_4C molecules corresponding to twelve boron and three carbon atoms (see Fig. 1). The three carbon atoms lie on the trigonal axis of the rhombohedron which is the c axis of the hexagonal representation. With respect to the symmetry and coördination, the two outside positions of the carbon chain $2c$ are identical and different from the central one $1b$. $1b$ is the only unique position in the boron carbide unit cell and was found to accommodate boron as well as carbon.[11] Thus the -C-C-C- chain can transform into -C-B-C- arrangement.[12] Complete substitution of carbon by boron in $1b$ position results in the ratio of $B_{13}C_2$.[5,6] The homogeneity range in the boron-carbon system is thus explained as a complete series of solid solutions between B_4C and $B_{13}C_2$.

Closely related to the above described structure is one of the recently reported modifications of boron.[7,8] While the framework of boron icosahedra appears to be identical with that found in boron carbide, the three carbon positions are vacant and represent interstitial openings. The rhombo-hedral unit cell thus contains 12 rather than 15 atoms of boron.

The large interstitial openings in boron suggest a possibility that the elements other than carbon may be accommodated in these positions forming a series of isostructural boron compounds.

The interstitial compounds (interstitial compounds are often referred to as interstitial solid solutions) are described in a simple way as involving the arrangement of relatively large metal atoms in closest packing or in some other simple structure and the insertion of the small non-metal atoms into interstices of the lattice of metal atoms.[13] The small atoms usually are found to be boron, carbon, nitrogen or oxygen. For example, the series of interstitial titanium compounds includes TiB, TiC, TiN and TiO.

The interstitial compounds of boron can be understood using the same description by considering the boron icosahedra as single units. Thus, the arrangement of boron icosahedra forms a somewhat distorted face centered cube, equivalent to the close packed atomic structure of large metal atoms. Since the icosahedra are large compared with the metal atoms, we find that as many as three non-metal atoms may be accommodated in the interstitial openings and the openings can accommodate larger elements of the second and third row of the periodic system as well as those of the first row.

Once the mechanism of formation of interstitial boron compounds is recognized, the isostructural compounds are identified easily by means of X-ray power photographs. In fact the identification of a series of these compounds consists in corrections of the known data rather than in the discovery of new compounds. The lower boron phosphide prepared by high temperature decomposition of BP, reported to have a chemical formula of B_6P^{14}, is properly identified on the basis of chemical analysis and X-ray data as $B_{13}P_2$.[4] Similarly, the high temperature decomposition product of BAs reported to have proportions of $B_{6-7}As^{14}$ and an orthorhombic unit cell[15] has been corrected[16] and found to have a corresponding rhombohedral unit cell containing one molecule of $B_{13}As_2$. The substitution system appears to include also the elements of the sixth group of the periodic system. Thus a lower boron oxide analyzed to be $B_{6.5}O$ and reported[17] as an orthorhombic B_7O also has been corrected[16] and found

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rhombohedral with the appropriate formula of $B_{13}O_2$. Thus the interstitial positions in boron structure are found to accommodate silicon, phosphorus, arsenic and oxygen as well as carbon, forming compounds isostructural either with B_4C or $B_{13}C_2$, depending on whether the 1b interstitial position is occupied by boron or the substitution element. The unit cell sizes of the above mentioned compounds are compared in Table I.

TABLE I

COMPARISON OF THE UNIT CELL SIZES OF THE INTERSTITIAL BORON COMPOUNDS

	Hexagonal cell			Rhombohedral cell	
	a, Å.	c, Å.	c/a	a. Å,	α
Boron	4.908	12.567	2.56	5.057	58° 4'
$B_{13}O_2$	5.37	12.31	2.30	5.14	62° 56'
$B_{12}C_3(B_4C)$	5.60	12.12	2.17	5.175	65° 18'
$B_{13}C_2$	5.67	12.19	2.15	5.218	65° 49'
$B_{13}P_2$	5.984	11.850	1.98	5.248	69° 31'
$B_{13}As_2$	6.142	11.892	1.935	5.319	70° 32'
$B_{12}Si_3(B_4Si)$	6.330	12.736	2.015	5.602	68° 49'

The compounds in Table I are arranged in the increasing order of the atomic sizes as we go down the table.[18] It is interesting that the expansion of the unit cell takes place in the direction of the hexagonal a-axis only. At the same time the unit cell shrinks in the direction of the c-axis until a certain minimum value is reached (about 11.85 Å.). From there on the expansion takes place in all directions. The rhombohedral unit cell expands accordingly by adjustment of the angle rather than by change of the axis size.

From the positions in the periodic table and on the basis of the atomic sizes it appears that at least two more interstitial boron compounds should exist: namely, a lower boron nitride and a lower boron sulfide.

Preparation of Boron Sulfide ($B_{12}S$).—Boron sulfide was prepared by the reaction of amorphous boron and sulfur powders at about 1600–1700°. The boron powder obtained from the United States Borax and Chemical Corporation was 95–97% pure. The sulfur powder was of U.S.P. quality and obtained from Merck and Company, Inc. The mixture of elements containing equal amounts of boron and sulfur by weight was pressed into a pellet, placed in a graphite crucible and fired in an induction furnace. The rate of heating is very important as the slow heating results in sublimation of sulfur, either in the elemental state or as B_2S_3, leaving boron as the residue. However, when a temperature of 1600–1700° is obtained within one or two minutes, a reaction between boron and sulfur takes place forming a fine brown or black powder. Upon further heating at 1600–1650°, the brown powder releases some sulfur and turns black. In order to avoid formation of boron carbide from reaction with the graphite crucible, the heating was discontinued as soon as a temperature of 1600–1700° was reached. The samples then were fired again in zirconia crucibles at about 1650° until evolution of sulfur vapors ceased and the sample appeared uniformly black. Heating

(18) Boron silicide is placed below boron arsenide, because the sum of sizes of three silicon atoms is larger than that of two atoms of arsenic and one of boron.
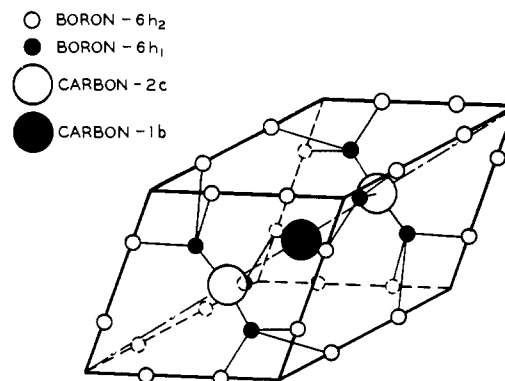
Fig. 1.—Rhombohedral unit cell of boron carbide (after Silver and Bray, ref. 11).

at above 1700° results in further evolution of sulfur leaving boron as the residue.

Measurement of temperatures was found to be exceedingly difficult as evolution of sulfur vapors interfered with the reading of the optical pyrometer. The temperatures therefore were estimated by running a blank under the same conditions.

Black samples obtained by above described procedure contained less than 1% and up to 2% carbon, with unreacted boron in some samples.

Chemical analysis of samples indicated a boron to sulfur ratio of 12:1. Somewhat higher ratios, up to 13:1, also were obtained, but they are explained by the presence of unreacted boron. The compound hence is assigned the formula of $B_{12}S$.

The X-ray powder photograph of $B_{12}S$ is very similar to that of $B_{13}P_2$ and is readily indexed (Table II) assuming a rhombohedral unit cell with hexagonal dimensions of a = 5.80 Å. and c = 11.90 Å. The corresponding rhombohedral dimensions are a = 5.19 Å. and α = 67° 56'. Density was determined by floating the powder in heavy liquids and by the pycnometer method. The measured value was found to be about 2.40 g./cm.[3] which is somewhat higher than the theoretical value of 2.33 g./cm.[3] calculated from X-ray data, assuming one $B_{12}S$ molecule per rhombohedral unit cell. Presence of about 2% carbon corresponds approximately to 9% B_4C or about 13% $B_{13}C_2$. As there is no evidence for the presence of boron carbide, it is assumed that a small amount of carbon is placed in the vacant interstitial openings in the $B_{12}S$ structure.

Discussion

The new lower boron sulfide, $B_{12}S$, while of different proportions belongs, on the basis of its structure, to the formerly described group of interstitial compounds of boron. The single atom of sulfur should logically be placed in the 1b position, since that is the only uniquely defined position in the structure. The two 2c positions therefore appear vacant and could possibly accommodate other elements such as carbon. The fact that the X-ray powder photographs do not show the presence of boron carbide even when up to 2% carbon is present indicates that this is the case. However, a defect structure also is possible.

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR $B_{12}S$

Obtained by use of 140 mm. camera and filtered CrKα radiation

h	k	l	d, Å.	I/I_1
0	0	3	3.97	20
0	1	2	3.84	70
1	1	0	2.90	10
1	0	4	2.566	100
0	2	1	2.454	100
0	1	5	2.159	10
2	1	1	1.875	10
1	1	6	1.641	10
3	0	3	1.545	5
1	2	5	1.486	30
2	2	0	1.449	20
2	0	3 }	1.413	20
1	0	8 }		
1	3	1	1.383	20
2	2	3 }	1.359	20
3	1	2 }		
2	0	8 }	1.283	50
3	0	6 }		
4	0	1	1.251	1
1	1	9 }	1.203	5
3	1	5 }		

With the discovery of $B_{12}S$ there appear to be three types of interstitial compounds of boron, namely, $B_{12}X$, $B_{12}X_3$ and $B_{13}X_2$.

The $2c$ positions in the structure are found to accommodate carbon, silicon, phosphorus and arsenic while the $1b$ position can accommodate boron, carbon, silicon and sulfur. A homogeneity range similar to that found in the boron–carbon system may also exist in some other boron systems. However, with the present methods of preparation they have not been observed.

Though the proposed mechanism explains satisfactorily the formation of a series of boron compounds involving elements of the third, fourth, fifth and sixth groups, a direct determination of the actual atomic arrangement would be desirable.[19] The X-ray scattering power of silicon, phosphorus, etc., is sufficiently different from that of boron to enable definite placement of these elements in the structure.

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(19) Such work is in progress at the Polytechnic Institute of Brooklyn by B. Post, on $B_{13}P_2$ crystals supplied by this Laboratory.

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The Donor Properties of Triphenylarsine Oxide

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The coördination chemistry of triphenylarsine oxide with a variety of acceptors has been investigated. The new substances $CrCl_3 \cdot 4R$, $CrCl_2ClO_4 \cdot 4R$, $MnCl_2 \cdot 2R$, $Mn(ClO_4)_2 \cdot 4R$, $FeCl_3 \cdot 2R$, $Fe(ClO_4)_3 \cdot 4R$, $CoCl_2 \cdot 2R$, $CoBr_2 \cdot 2R$, $Co(ClO_4)_2 \cdot 4R$, $NiCl_2 \cdot 2R$, $Ni(ClO_4)_2 \cdot 4R$, $Cu(NO_3)_2 \cdot 4R$, $Zn(ClO_4)_2 \cdot 4R$, $HgCl_2 \cdot 2R$, $HgCl_2 \cdot R$, $SnCl_4 \cdot 2R$, $SnBr_4 \cdot 2R$, $SbCl_3 \cdot 2R$, and $SbCl_5 \cdot R$ (where R = triphenylarsine oxide) have been isolated and characterized by molecular conductance measurements in nitrobenzene, cryoscopic molecular weight measurements in freezing nitrobenzene, magnetic susceptibility measurements and infrared spectra. Most of the halides appear to be non-electrolytes, whereas the nitrate and perchlorates appear to be salt-like.

Introduction

In the course of some previous work we became aware of the class of compounds formed between triphenylphosphine oxide and metal halide acceptors.[1] Now we wish to report extensions of the earlier work to a wider variety of metal compounds and using triphenylarsine oxide. During the course of the work two other laboratories[2] reported analogous series of phosphine oxide compounds. Also Lindquist[3] has prepared and studied some additional similar phosphine oxide complexes in the interim. Workers in Prof. Hieber's laboratory at Munich also report addition compounds of iron and cobalt carbonyls with triphenylarsine oxide.[4,5]

We believe the first example of an arsine oxide complex to be $(C_3H_7)_3AsO \cdot 2HgCl_2$, reported by Partheil and co-workers.[6] The only other examples we are aware of are $Cu[(C_6H_5)_2CH_3AsO]_4X_2$, reported by Nyholm,[7] and the chelates bis-(α-picolyldimethylarsine oxide)-copper(I) perchlorate and bis-(α-picolyldimethylarsine oxide)-copper(II) perchlorate, reported by Goodwin and Lions.[8]

Experimental

Reagents.—Reagent grade chemicals were used without further purification except in the cases noted.

Triphenylarsine oxide was prepared from Eastman "White Label" triphenylarsine,[9] m.p. 194.5–196°; literature values, 189°[10,11] and 191–193°.[12]

Anal. Calcd. for $(C_6H_5)_3AsO$: As, 23.25. Found[13]: As, 23.0.

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