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Group IV Analogs and High Pressure, High Temperature Synthesis of B_2O[1]

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An "unsymmetrical" analog of graphite, B_2O, has been synthesized by reduction of B_2O with B and Li and also by the oxidation of B with $KClO_3$. Application of pressures ranging from about 50,000 to 75,000 atm. combined with temperatures from about 1200 to 1800° is required for these syntheses. The new B_2O compound has hexagonal crystal symmetry with a = 7.98 and c = 9.09 Å. and has a density of about 2.24 g./cm.^{3}. The synthesis of this new material points up the possibility of synthesizing a host of other unsymmetrical group IV analogs that have heretofore been overlooked. These analogs have the following unit formulas when two kinds of atoms are involved: $I-V_3$, I_2-VI_3, $II-V_2$, II_3-VII_2, III_2-VI, and III_3-VII. The well-known symmetrical group IV analogs, of course, have the unit formulas I–VII, II–VI, and III–V.

Introduction

The elements with principal quantum number n = 2 (Li, Be, B, C, N, O, F) exhibit a tendency to form strongly directed bonds, particularly tetrahedral bonds, when the electronegativity difference ΔX between combining atoms is not too large. Diamond is the foremost example of a tetrahedrally-bonded, crystalline structure, and, after about 125 years of scientific effort, was finally synthesized in the year 1954.[2] The first synthesis utilized a catalyst together with high pressure and temperature to convert graphite to diamond. Several years later, graphite was converted directly to diamond without the aid of a catalyst by dynamic pressure[3] and also by static pressure[4] at high temperature. Much higher pressures and temperatures were required in the direct conversion than when a catalyst was present.

The compound BN (ΔX = 1.0) has long been known in a hexagonal, layer-lattice form related to graphite. This material was converted to a diamond-like form by means of high pressure and high temperature in the presence of a catalyst just a few years ago.[5] Still more recently the diamond-like form of BN was prepared directly from the hexagonal form by utilizing higher pressures and temperatures than were needed when a catalyst was used.[6]

The compound BeO (ΔX = 2.0) is only known in one crystalline form—a hexagonal wurtzite structure in which tetrahedral bonding prevails. It is likely, however, that the bonding in BeO is somewhat more ionic than covalent. The compound LiF (ΔX = 3.0) is known only in an octahedrally coordinated rock salt structure in which the bonding is essentially ionic.

The three compounds BN, BeO, and LiF are composed of elements symmetrically arranged each side of carbon in the periodic table. These compounds are isoelectronic with carbon; *i.e.*, the average number of valence electrons per atom is four. Consequently, they tend to simulate the properties of carbon. The compound BN, being closest to carbon, and having the smallest ΔX, imitates the properties of carbon quite well. Some properties of carbon (in the diamond form) are moderately well-displayed in BeO, while LiF bears very little resemblance to either the graphite or diamond forms of carbon.

In recent years, silicon and germanium have assumed great importance because of their semiconducting properties. These properties are intimately dependent upon the tetrahedral bonding that exists in crystals of these elements. To obtain other semiconducting materials that simulate the properties of silicon and germanium or other group IV elements, such tetrahedrally bonded substances as AlP, GaAs, ZnS, CdTe, InSb, and AgI have been prepared. High pressure is not needed to synthesize any of the known I–VII, II–VI, and III–V compounds (group IV analogs) other than diamond-like BN.

Unsymmetrical Carbon Analogs

The above "symmetrical" group IV analogs are a relatively obvious type of compound and much work has been done on their synthesis and properties. The less obvious, "unsymmetrical" group IV analogs, however, have apparently never before been considered. The unsymmetrical carbon analogs are listed in Table I together with ΔX. The symmetrical isoelectronic analogs are also listed for comparison.

TABLE I
ISOELECTRONIC, TWO-ATOM ANALOGS OF CARBON
LISTED WITH ΔX

Symmetrical		Unsymmetrical			
BN	(1.0)	B_2O	(1.5)	B_3F	(2.0)
BeO	(2.0)	BeN_2	(1.5)	Be_3F_2	(2.5)
LiF	(3.0)	LiN_3	(2.0)	Li_2O_3	(2.5)

Synthesis of B_2O

The authors have succeeded in preparing the unsymmetrical compound B_2O as a graphite analog by high pressure, high temperature methods. Attempts to make this new material at 1 atm. have not met with

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(1) Presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 4–9, 1965.

(2) F. P. Bundy, H. T. Hall, H. M. Strong, and R. H. Wentorf, Jr., *Nature*, **176**, 51 (1955); H. P. Bovenkerk, F. P. Bundy, H. T. Hall, H. M. Strong, and R. H. Wentorf, Jr., *ibid.*, **184**, 1094 (1959); H. T. Hall, *J. Chem. Educ.*, **38**, 484 (1961).

(3) P. S. DeCarli and J. C. Jamieson, *Science*, **133**, 1821 (1961).

(4) F. P. Bundy, *ibid.*, **137**, 1057 (1962).

(5) R. H. Wentorf, Jr., *J. Chem. Phys.*, **34**, 809 (1961).

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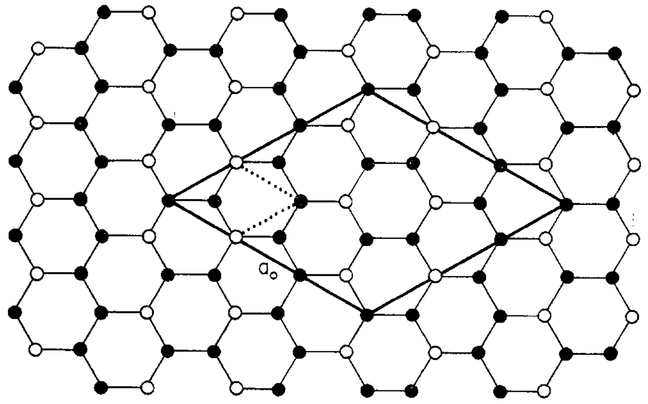

Figure 1.—A possible hexagonal lattice for B_2O. Open circles represent the centers of oxygen atoms; solid circles the centers for boron.

success. The high pressure, high temperature synthesis has been accomplished by reducing B_2O_3 with B or Li and also by oxidizing B with $KClO_3$. A convenient synthesis utilizes a mixture of B and B_2O_3 powders in the reaction $4B + B_2O_3 \rightarrow 3B_2O$. The reacting powders are ground together for 24 hr. in a ball mill and are then compressed into a small cylindrical specimen for use in the Tetrahedral Press.[7,8] The specimen is contained in a hexagonal BN capsule and is indirectly heated. The pyrophyllite tetrahedral cell geometry and resistance strip-heater arrangement have been described elsewhere.[9] Pressures from about 50,000 to 75,000 atm. are used at temperatures from about 1200 to 1800°. After pressure has been applied, the temperature is increased to the desired value in about 5 sec. Temperature is held for about 3 min. and then the heating current is switched off to quench the product to room temperature. The product is light reddish brown in color and has a measured density of 2.24 ± 0.04 g./cm.^{3} Powder X-ray diffraction patterns indicate hexagonal crystal symmetry with unit cell dimensions a = 7.98 and c = 9.09 Å. This, together with the density, suggests a layer-lattice structure related to graphite.

A hexagonal layer of a possible B_2O lattice is shown in Figure 1. A second identical layer could be located above the first layer a distance of $c/3$ but shifted along the a axis by the distance $a/3$. A third layer could be similarly spaced and shifted above the second layer to give an ...ABCABC... layer repeat. The theoretical density of this structure would be 2.24 g./cm.^{3}, which agrees with the measured B_2O density. The suggested unit cell contains 36 boron and 18 oxygen atoms. In this structure, a for B_2O is 8% longer than $3a$ for graphite and c for B_2O is 10% shorter than the value of c for "rhombohedral" graphite. In moving along the a direction of the hexagonal layer lattice depicted in Figure 1, it is noted that the linear atom sequence is ...BOBBOBBOB..., which corresponds to the unit formula B_2O and gives a sequential repeat after every third atom. In graphite, the corresponding sequence is ...CCCCCCCCC..., which, of course, gives a repeat after very carbon atom. Consequently, the a axis repeat distance in graphite is only about one-third of that for B_2O and the graphite layer cell (completed by the dotted lines) has only about one-ninth the area of the B_2O layer cell. For comparison, structural data for "rhombohedral" graphite, hexagonal BN, and hexagonal B_2O are given in Table II.

TABLE II
STRUCTURAL DATA FOR RHOMBOHEDRAL GRAPHITE AND HEXAGONAL BN AND B_2O

Substance	a, Å.	c, Å.	Inter-planar spacing, Å.	Av. atom–atom dist. in plane, Å.
Rhombohedral graphite	2.45	10.05	3.35	1.42
Hexagonal BN	2.50	6.66	3.33	1.45
Hexagonal B_2O	7.98	9.09	3.03	1.54

Pressures of about 120,000 atm. have been utilized in attempts to synthesize a diamond-like form of B_2O. So far, faint indications of a diamond-like form have been evident in some powder X-ray diffraction patterns and in scratch tests. Although this evidence is quite inconclusive, a final, clean-cut synthesis of diamond-like B_2O is expected to be achieved. It is also contemplated that graphite and diamond-like forms of BeN_2, which is symmetrically related to B_2O, will eventually be synthesized. For the compounds LiN_3 and B_3F, ΔX = 2, the same value as for BeO. Therefore, tetrahedral bonding may be possible in these compounds. As is the case with BeO, however, the bonding would probably be more ionic than covalent. In Li_2O_3 and Be_3F_2, ΔX = 2.5. This large difference in electronegativity may preclude the formation of diamond-like or graphite-like bonds under ordinary circumstances. However, high pressure tends to decrease and level electronegativities and consequently lowers ΔX values. This lowering of ΔX would favor the formation of covalent bonds at a sufficiently high pressure. Thus, if diamond- or graphite-like bonds were formed at high pressure and temperature, they might survive a return to room temperature and pressure. At a sufficiently high pressure, even LiF, with ΔX = 3, might assume appreciable covalent bonding. However, covalently-bonded LiF could probably not remain as a metastable entity at atmospheric pressure.

Silicon Analogs

What has been said above, in a general way, for carbon analogs also holds for silicon and for other group IV elements. For reference, the silicon analogs, together with ΔX, are listed in Table III. The symmetrical compounds AlP (tetrahedrally-bonded, sphalerite structure), MgS (rock salt structure), and NaCl (rock salt) are all well-known. However, none of the unsymmetrical compounds is known. With the increased metallicity of the n = 3 period, the tendency to form strong, directed bonds probably disappears when ΔX exceeds 1.5. An increase in principal quan-

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(9) H. T. Hall and L. Merrill, *Inorg. Chem.*, **2**, 618 (1963).

TABLE III

ISOELECTRONIC, TWO-ATOM ANALOGS OF SILICON LISTED WITH ΔX

AlP	(0.6)	Al_2S	(1.0)	Al_3Cl	(1.5)
MgP_2	(0.9)	MgS	(1.3)	Mg_3Cl_2	(1.8)
NaP_3	(1.3)	Na_2S_3	(1.6)	NaCl	(2.1)

trum number increases the degree of metallization of a bond and decreases bond directionality.[10] The compounds MgP_2, NaP_3, Al_2S, MgS, and Al_3Cl should be capable of forming covalent, directionally-bonded structures. Attempts to prepare them from stoichiometric mixtures of the elements under high pressure, high temperature conditions would certainly be worthwhile. It might be noted here that catalysts might be efficacious in these syntheses. This is certainly true in the synthesis of diamond and of diamond-like BN. However, experience with catalysts in high pressure synthesis is very limited and no guidelines can be offered to the interested researcher. Suffice it to say that molten transition metals aid diamond synthesis from graphite, alkali and alkaline earth metals and nitrides aid the synthesis of diamond-like BN from hexagonal BN, and water and a host of low melting salts and oxides assist in the formation of dense forms of SiO_2 and silicate minerals from less dense reactants. The remaining compounds of Table III, Mg_3Cl_2 and Na_2S_3, might form strong directed bonds under sufficiently high pressure but would not likely survive a return to atmospheric pressure.

Cross Compounds

There is, of course, a possible series of group IV "cross compound" analogs between the elements of $n = 2$ and $n = 3$, between those of $n = 2$ and $n = 4$, and so on. An average principal quantum number $\bar{n}$ for cross compounds, where n_i is the principal quantum number of an atom of kind i and c_i is the number, per formula unit, of atoms of this kind, can be assigned as follows: $\bar{n} = \Sigma c_i n_i / \Sigma c_i$.[10] Cross compounds of $n = 2$ and $n = 3$ atoms, together with $\bar{n}$ and ΔX, are listed in Table IV.

TABLE IV

CROSS COMPOUNDS, COMPOSED OF ELEMENTS WITH $n = 2$ AND $n = 3$

Compd.	ΔX	$\bar{n}$	Compd.	ΔX	$\bar{n}$
LiCl	2.0	2.5	NaF	3.1	2.5
Li_2S_3	1.5	2.6	Na_2O_3	2.6	2.4
LiP_3	1.1	2.8	NaN_3	2.1	2.2
Be_3Cl_2	1.5	2.4	Mg_3F_2	2.8	2.6
BeS	1.0	2.5	MgO	2.3	2.5
BeP_2	0.6	2.7	MgN_2	1.8	2.3
B_3Cl	1.0	2.2	Al_3F	2.5	2.8
B_2S	0.5	2.3	Al_2O	2.0	2.7
BP	0.1	2.5	AlN	1.5	2.5
CSi	0.7	2.5	SiC	0.7	2.5

The symmetrical compounds SiC, BP, AlN, and BeS and the unsymmetrical compound NaN_3 are all known in structures possessing tetrahedral bonding. These can all be prepared at atmospheric pressure. However, some of them can be prepared more conveniently under high pressure, high temperature conditions. The high pressure product is usually more crystalline and the macroscopic density more nearly approaches the theoretical (X-ray) density than products formed at 1 atm. Crystalline BP, for example, is easily synthesized from the intimately mixed elements at about 10,000 atm. at temperatures around 1500°. These conditions are very easily achieved in an internally heated Tetrahedral Press, Belt, or Piston-Cylinder apparatus.

The well-known compounds MgO, LiCl, and NaF crystallize in the rock salt structure. None of the remaining compounds in Table IV is presently known. Other things being equal, the strongest directed bonds would be expected to form in cross compounds having small values of both $\bar{n}$ and ΔX. Consequently B_2S and B_3Cl (Table IV) are particularly good candidates for attempted synthesis in graphite or diamond-like forms. The compounds Be_3Cl_2, MgN_2, and BeP_2 would be expected to form reasonably strong directed bonds, while Li_2S_3, LiP_3, and perhaps Al_2O would form weaker directed bonds. The remaining compounds would be poor candidates for possible synthesis as group IV analogs.

Conclusions

The proposed, directionally-bonded compounds discussed above would have relatively high melting or sublimation temperatures, high hardness and high thermal conductivity (in tetrahedrally bonded structures), and good semiconducting properties. Additional tables of group IV analogs (similar to Tables I, III, and IV) can be constructed by involving $n = 4$, 5, 6, and 7 atoms and by considering the "B" periodic grouping of elements as well as the "A." The above ideas can also be extended to include more than two kinds of atoms in a compound. This greatly increases the number of isoelectronic types. For example, if three different kinds of atoms with $n = 2$ are used to make carbon analogs there are 27 possible compounds. (With two kinds of atoms there are only 9 possible compounds.)

The above group IV analogs should prove to be of interest to the high pressure researcher for a number of reasons: (1) Only a limited number of these compounds are known. Conventional synthesis techniques have not produced them. Therefore, it would seem worthwhile to utilize the newly available tool of high pressure, high temperature to attempt their synthesis. (2) Diamond and diamond-like BN and probably hexagonal B_2O are thermodynamically stable only at high pressure. Consequently, high pressure is required for their synthesis. Rate considerations allow these materials to remain in a metastable state under room conditions when once formed. It is anticipated that many of the proposed compounds will also only be stable while under high pressure. High temperature is also required because the breaking and forming of

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(10) E. Mooser and W. B. Pearson, *Acta Cryst.*, **12**, 1015 (1959).

strong, directed bonds is involved. Such bonds are only mobile at high temperature and, in addition, often require the presence of a catalyst to orient atoms for bond formation properly. (3) Regardless of the thermodynamic requirements for the synthesis of a given group IV analog, high pressure is often required just to "contain" reactants which may be quite volatile at the required temperature. Today's high pressure, high temperature equipment is admirably capable of doing this job. Substances such as sulfur are easily contained at temperatures of 1500°.

It is hoped that this paper, in calling attention to the unsymmetrical group IV analogs, will incite inorganic chemists to attempt their synthesis. These compounds far outnumber the symmetrical analogs and should be very important to solid state technology.

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Chemistry of Boranes.[1] XXV. Synthesis and Chemistry of Base Derivatives of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$

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A series of new base derivatives of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ has been prepared from the acid-catalyzed reaction of certain Lewis bases with the parent anions. These derivatives have the composition $B_{10}H_9L^-$, $B_{12}H_{11}L^-$, $B_{10}H_8L_2$, and $B_{12}H_{10}L_2$ in which the ligand may be sulfone, sulfonamide, urea, nitrile, nitrobenzene, or iodobenzene. The stereochemistry of these reactions has been qualitatively assayed. The reactivity of these base derivatives toward electrophilic reagents, such as D_3O^+ and halogen, is lower than that of the parent ions.

Previous papers dealing with the derivative chemistry of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ described derivatives in which one or two hydride ions had been replaced by common Lewis base ligands such as amines, carboxamides, sulfides, phosphines, and arsines and also by nitrogen and carbon monoxide.[1-10] We have found that other Lewis base derivatives of the polyhedral borane anions can be prepared by acid-catalyzed reactions of these anions with sulfones, sulfonamides, nitriles, amides, or nitrobenzene. The synthesis of these new base derivatives and a comparison of their properties with those of the previously described base derivatives are the subjects of this paper.

Synthesis.—Under acidic conditions, the $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ ions react with certain Lewis bases to give hydrogen and $B_{10}H_9L^-$ or $B_{12}H_{11}L^-$ species. Reaction

$$H^+ + B_{12}H_{12}^{2-} + L \longrightarrow H_2 + B_{12}H_{11}L^- \qquad (1)$$

rate varies with the nature of L and is a direct function of acid concentration. Water markedly reduces the reaction rate. For example, sulfone reactions proceed at 25° if water is essentially absent; but, if significant amounts of water are present, moderate reaction rates are not achieved until the temperature is raised to 70–90°. We believe (*vide infra*) that protonated forms of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ are reaction intermediates in (1), and this is consistent with the rate-dependence on acid and water concentrations because the polyhedral borane ions are the conjugate bases of very strong acids.[11]

Under forcing conditions, the monobase derivatives react further with base to give the neutral derivatives

$$H^+ + B_{12}H_{11}L^- + L \longrightarrow H_2 + B_{12}H_{10}L_2 \qquad (2)$$

The course of the base–borane reaction can be accurately followed by the hydrogen evolution since in general the activation energies for reactions 1 and 2 are significantly different for a given base. This difference may be attributable to the relative ease of protonation of $B_{12}H_{12}^{2-}$ and $B_{12}H_{11}L^-$.

Operable Lewis bases for reactions 1 and 2 are sulfones, sulfonamides, tetramethylurea, nitriles, and nitrobenzene. Under nearly anhydrous conditions, amides react in a similar fashion.[5] As discussed below, we believe the linkage is B–O in sulfone, amide, tetramethylurea, and nitrobenzene derivatives and B–N in sulfonamide and nitrile derivatives. Thus it appears

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