

result may have been due in part to steric factors, however.

The ^1H nmr chemical shifts of the vinyl protons in carboranes I and II are found to be intermediate between normal benzenoid and olefinic regions. This effect can now most probably be attributed to deshielding due to the inductive electron withdrawal of the cage.^{1,12}

Thus, even though there is some evidence of alkene

(12) K. M. Harmon, A. B. Harmon, and B. C. Thompson, *J. Amer. Chem. Soc.*, **89**, 5309 (1967).

group delocalization into the face of the substituted (3)-1,2- $\text{B}_9\text{C}_2\text{H}_{12}^-$ ions, these compounds have so far largely paralleled other substituted carboranes in their derivative chemistry.

Acknowledgment—The authors wish to express their gratitude to Professor F. A. L. Anet, Mr. Craig Bradley, and Dr. Richard Wiersema of this department for the 250-Mc/sec pmr and 80-Mc/sec boron nmr spectra. This research was supported, in part, by the Office of Naval Research.

CONTRIBUTION FROM THE ARCADIA INSTITUTE FOR SCIENTIFIC RESEARCH,
135 NORTHRIDGE LANE, WOODSIDE, CALIFORNIA 94062

The Structon Theory, Applied to Crystalline Borates¹

By MAURICE L. HUGGINS

Received July 20, 1970

Principles and generalizations, previously applied to crystalline silicates and related compounds, are now applied to crystalline anhydrous borates. Many of these contain boron atoms with only three oxygen neighbors; some contain oxygen atoms with three boron neighbors. The types of *structons* and the relative numbers of these types are presented for the compounds of known crystal structure. It is shown how these data are related to the oxygen:boron ratio, the effective charges on the oxygen atoms, and equilibria between sets of structon types.

Introduction

This is one of a series of papers²⁻⁴ dealing with principles of the structure of crystals and glasses. The present contribution is concerned with anhydrous crystalline borates.

In the structon theory⁵⁻⁷ emphasis is placed on the closest neighbor arrangements, *i.e.*, on the types of structons present, the relative numbers of these types, and their properties: their contributions to the overall properties of the substance and their effects on the arrangements of nonclosest-neighbor atoms.

It is useful to express the composition of a substance or an anion by a normalized formula, giving the numbers of the component atoms per *G-type atom* (in this case, per B). Thus, boric oxide, B_2O_3 , is represented by the normalized formula $\text{BO}_{1.5}$ and the compound CdB_4O_7 is represented by the normalized formula $\text{Cd}_{0.25}\text{BO}_{1.75}$. The anion in that compound has the normalized formula $\text{BO}_{1.75}^{0.50-}$. The general formula for this and other borate anions can be written $\text{BO}_\sigma^{\rho-}$, with σ designating the number of oxygen atoms per boron atom and ρ designating the number of units of negative charge per boron atom. In an alkali borate, $\text{M}_2\text{O} \cdot \text{B}_2\text{O}_3$, ρ is also the number of moles of alkali oxide per mole of boric oxide. The number of metal cations (M) per

boron atom is ρ in an alkali borate and $\rho/2$ in an alkaline earth borate. Neutrality for the whole substance requires that

$$\rho = 2\sigma - 3 \quad \sigma = \frac{3}{2} + \frac{\rho}{2} \quad (1)$$

Structon Types

The types of structons and the relative numbers of these types in a crystalline compound can be deduced from the locations of the atoms, as determined by crystal analysis. Table I lists the structon types for boric oxide and all borates of known structure. Each structon type is represented by a *structon formula*, in which the symbol for the structon atom is given first, followed in parentheses by symbols and numbers indicating the environment of closest neighbors. The structon formulas are enclosed in angular brackets ($\langle \rangle$) to distinguish them from ordinary chemical formulas. The metal cations are all represented by the symbol M. The numbers, per boron atom, of each structon type are given before the structon formulas.

Table I also gives the normalized formulas for the borate anions (or the macromolecules in the case of boric oxide), with references to the literature, to the bond diagrams for the motifs of the anion structures (Table II), and to the appropriate sets of structon types in Table VII.

Each motif in Table II shows the unit of the pattern of interatomic bonds in the anion (or polymer molecule, in B_2O_3) but not the arrangement of atoms and bonds in space. Only half of each O'' oxygen represented as

(1) Presented at the Buffalo Meeting of the American Crystallographic Association, Aug 15, 1968.

(2) M. L. Huggins, *Macromolecules*, **1**, 184 (1968).

(3) M. L. Huggins, *Inorg. Chem.*, **7**, 2108 (1968).

(4) M. L. Huggins, *Acta Crystallogr., Sect. B*, **26**, 219 (1970).

(5) M. L. Huggins, *J. Phys. Chem.*, **58**, 1141 (1954).

(6) M. L. Huggins, *J. Amer. Ceram. Soc.*, **38**, 172 (1955).

(7) M. L. Huggins, *Bull. Chem. Soc. Jap.*, **28**, 606 (1927).

TABLE I
STRUCTONS IN CRYSTALLINE BORATES

Conventional formula	Normalized formula of anion	Ref	Motif	Set	Boron structons	Cation structons	Oxygen structons
B ₂ O ₃ (I)	BO _{1.5}	<i>a</i>	I	1	1(B ₃ (30''))		1.50(O''(2B ₃)) ₀
B ₂ O ₃ (II)	BO _{1.5}	<i>b, c</i>	II	12	1(B ₃ (O'', 30''))		0.50(O''(2B ₃)) _{0.50-} , 1(O'''(3B ₄)) _{0.35+}
CsB ₃ O ₄	BO _{1.50} ^{0.11-}	<i>d</i>	III	2	0.89(B ₃ (30'')), 0.11(B ₄ (40''))	0.11(M(100''))	0.44(O''(2B ₃)) ₀ , 0.67(O''(2B ₃ , M)) _{0.10+} , 0.44(O''(B ₃ , M)) _{0.15-}
KB ₃ O ₈	BO _{1.60} ^{0.20-}	<i>e</i>	IV	2	0.80(B ₃ (30'')), 0.20(B ₄ (40''))	0.20(M(70''))	0.40(O''(2B ₃)) ₀ , 0.40(O''(2B ₃ , M)) _{0.14+} , 0.60(O''(B ₃ , B ₄ , M)) _{0.11-}
RbB ₃ O ₈	BO _{1.60} ^{0.20-}	<i>f</i>	IV	2	0.80(B ₃ (30'')), 0.20(B ₄ (40''))	0.20(M(70''))	0.20(O''(B ₃ , B ₄ , 2M)) _{0.04+}
Na ₂ B ₈ O ₁₃	BO _{1.625} ^{0.25-}	<i>g</i>	V	2	0.75(B ₃ (30'')), 0.25(B ₄ (40''))	0.13(M(70'')), 0.13(M(80''))	0.40(O''(2B ₃ , M)) _{0.14+} , 0.40(O''(2B ₃ , M)) _{0.14+} , 0.60(O''(B ₃ , B ₄ , M)) _{0.11-}
Ag ₅ B ₈ O ₁₃	BO _{1.625} ^{0.25-}	<i>h</i>	V	2	0.75(B ₃ (30'')), 0.25(B ₄ (40''))	0.13(M(70'')), 0.13(M(80''))	0.20(O''(B ₃ , B ₄ , 2M)) _{0.04+}
CsB ₃ O ₅	BO _{1.667} ^{0.33-}	<i>i</i>	VI	2	0.67(B ₃ (30'')), 0.33(B ₄ (40''))	0.33(M(20''))	0.50(O''(2B ₃ , M)) _{0.13+} , 0.13(O''(2B ₃ , 2M)) _{0.27+} , 0.88(O''(B ₃ , B ₄ , M)) _{0.12-}
Li ₂ B ₄ O ₇	BO _{1.75} ^{0.50-}	<i>j</i>	VII	4	0.50(B ₃ (30'')), 0.50(B ₄ (40''))	0.50(M(50''))	0.63(O''(2B ₃ , M)) _{0.14+} , 0.75(O''(B ₃ , B ₄ , M)) _{0.12-} , 0.25-(O''(B ₃ , B ₄ , 2M)) _{0.01+}
CdB ₄ O ₇	BO _{1.75} ^{0.50-}	<i>k</i>	VII	4	0.50(B ₃ (30'')), 0.50(B ₄ (40''))	0.25(M(70''))	0.33(O''(2B ₃ , 2M)), 1.33(O''(B ₃ , B ₄ , 2M))
BaB ₄ O ₇	BO _{1.75} ^{0.50-}	<i>l</i>	VIII	0.50(B ₃ (30'')), 0.50(B ₄ (40''))	0.13(M(90'')), 0.13(M(100''))	0.13(O''(2B ₃ , M)) _{0.05-} , 0.50(O''(B ₃ , B ₄ , 2M)) _{0.15+} , 0.25-(O''(2B ₃ , 2M)) _{0.10-}	
SrB ₄ O ₇	BO _{1.75} ^{0.50-}	<i>m</i>	IX	15	0.50(B ₄ (30'', O'')), 0.50(B ₄ (20'', 20''))	0.25(M(90''))	1.50(O''(B ₃ , B ₄ , M)) _{0.01+} , 0.25(O''(2B ₄ , M)) _{0.21-}
PbB ₄ O ₇	BO _{1.75} ^{0.50-}	<i>m</i>	IX	15	0.50(B ₄ (30'', O'')), 0.50(B ₄ (20'', 20''))	0.25(M(90''))	0.13(O''(2B ₃ , M)) _{0.20+} , 1(O''(B ₃ , B ₄ , M)) _{0.04-} , 0.25(O''(B ₃ , B ₄ , 2M)) _{0.17+}
LiBO ₂ (I)	BO ₂ ¹⁻	<i>n</i>	X	7	1(B ₃ (O', 20''))	1(M(40', O''))	0.38(O''(2B ₄ , 2M)) _{0.08-}
LiBO ₂ (III)	BO ₂ ¹⁻	<i>o</i>	XI	5	1(B ₄ (40''))	1(M(40''))	0.25(O''(2B ₄ , M)) _{0.28-} , 1(O''(2B ₄ , 2M)) _{0.06-} , 0.50(O''(3B ₄)) _{0.25+}
NaBO ₂	BO ₂ ¹⁻	<i>p</i>	XII	7	1(B ₃ (O', 20''))	1(M(50', 20''))	0.25(O''(2B ₄ , M)) _{0.28-} , 1(O''(2B ₄ , 2M)) _{0.06-} , 0.50(O''(3B ₄)) _{0.25+}
KBO ₂	BO ₂ ¹⁻	<i>q</i>	XII	7	1(B ₃ (O', 20''))	1(M(50', 20''))	1(O'(B ₃ , 4M)) _{0.20-} , 1(O''(2B ₃ , M)) _{0.20+}
CaB ₂ O ₄ (I)	BO ₂ ¹⁻	<i>r</i>	X	7	1(B ₃ (O', 20''))	0.50(M(60', 20''))	1(O'(B ₃ , 5M)) _{0.29-} , 1(O''(2B ₃ , 2M)) _{0.29+}
CaB ₂ O ₄ (III)	BO ₂ ¹⁻	<i>s</i>	XIII	0.17(B ₃ (20', O'')), 0.17(B ₃ (30''))	0.17(M(20', 60''))	0.17(M(20', 60''))	1(O'(B ₃ , 3M)) _{0.25-} , 1(O''(2B ₃ , M)) _{0.25+}
CaB ₂ O ₄ (IV)	BO ₂ ¹⁻	<i>t</i>	XIV	5	1(B ₄ (40''))	0.17(M(20', 80''))	0.17(O'(B ₃ , 2M)) _{0.35-} , 0.17(O'(B ₃ , 3M)) _{0.30-} , 0.50(O''(B ₃ , B ₄ , 2M)) _{0.23+}
SrB ₂ O ₄ (I)	BO ₂ ¹⁻	<i>u</i>	X	7	1(B ₃ (O', 20''))	0.50(M(120''))	0.17(O''(B ₃ , B ₄ , 3M)) _{0.45+} , 1(O''(2B ₄ , 2M)) _{0.05-}
SrB ₂ O ₄ (III)	BO ₂ ¹⁻	<i>v</i>	XIII	0.17(B ₃ (20', O'')), 0.17(B ₃ (30''))	0.17(M(20', 60''))	0.17(M(20', 60''))	2(O''(2B ₄ , 3M)) ₀
SrB ₂ O ₄ (IV)	BO ₂ ¹⁻	<i>v</i>	XIV	5	1(B ₄ (40''))	0.17(M(20', 80''))	1(O'(B ₃ , 3M)) _{0.25-} , 1(O''(2B ₃ , M)) _{0.25+}
BaB ₂ O ₄ (II)	BO ₂ ¹⁻	<i>w</i>	XII	7	1(B ₃ (O', 20''))	0.17(M(60', 30''))	0.17(O'(B ₃ , 2M)) _{0.35-} , 0.17(O'(B ₃ , 3M)) _{0.45+} , 0.50(O''(B ₃ , B ₄ , 2M)) _{0.05-}

$Mg_2B_2O_3$	BO_3, s^2-	x	XV	9	$1(B_4(2O', O''))$	$0.50(M(6O')), 0.50(M(5O', O''))$	$0.50(O'(B_3, 2M))_{0.33-}, 1.50(O'(B_3, 3M))_0, 0.50(O''(2B_3, M))_{0.33+}$
$Co_2B_2O_5$	BO_3, s^2-	y	XV	9	$1(B_4(2O', O''))$	$0.50(M(6O')), 0.50(M(5O', O''))$	$0.50(O'(B_3, 2M))_{0.33-}, 1.50(O'(B_3, 3M))_0, 0.50(O''(2B_3, M))_{0.33+}$
$Mg_3B_2O_4$	BO_3, s^2-	s-bb	XVI	11	$1(B_4(3O'))$	$1.50(M(6O'))$	$3(O'(B_3, 3M))_0$
$Co_3B_2O_6$	BO_3, s^2-	aa	XVI	11	$1(B_4(3O'))$	$1.50(M(6O'))$	$3(O'(B_3, 3M))_0$
$LnAl_3B_4O_{13}$	BO_3, s^2-	cc-ee	XVI	11	$1(B_4(3O'))$	$0.25(M(6O')), 0.75(M(6O'))$	$1.50(O'(B_3, 2M'))_0, 1.50(O'(B_3, M, M'))_0$
$LnGa_3B_4O_{13}$	BO_3, s^2-	ee	XVI	11	$1(B_4(3O'))$	$0.25(M(6O')), 0.75(M(6O'))$	$1.50(O'(B_3, 2M'))_0, 1.50(O'(B_3, M, M'))_0$
$LnCr_3B_4O_{13}$	BO_3, s^2-	cc, dd	XVI	11	$1(B_4(3O'))$	$0.25(M(6O')), 0.75(M(6O'))$	$1.50(O'(B_3, 2M'))_0, 1.50(O'(B_3, M, M'))_0$

^a S. L. Strong and R. Kaplow, *Acta Crystallogr.*, Sect. B, **24**, 1032 (1968). ^b G. E. Curr, P. W. Montgomery, C. D. Knutson, and B. T. Corres, paper presented at the meeting of the American Crystallographic Association, Minneapolis, Minn., Aug 1967. ^c O. T. Prewitt and R. D. Shannon, *Acta Crystallogr.*, Sect. B, **24**, 869 (1968). ^d J. Krogh-Moe and M. Ihara, *ibid.*, **23**, 427 (1967). ^e J. Krogh-Moe, *ibid.*, **18**, 1088 (1965). ^f J. Krogh-Moe, *Ark. Kemi*, **14**, 439 (1959). ^g A. Hyman, A. Perloff, F. Maurer, and S. Block, *Acta Crystallogr.*, **22**, 815 (1967). ^h J. Krogh-Moe, *ibid.*, **18**, 77 (1965). ⁱ J. Krogh-Moe, *ibid.*, **13**, 889 (1960). ^j J. Krogh-Moe, *ibid.*, **15**, 190 (1962). ^k M. Ihara and J. Krogh-Moe, *ibid.*, **20**, 132 (1966). ^l S. Block and A. Perloff, *ibid.*, **19**, 297 (1965). ^m A. Perloff and S. Block, *ibid.*, **20**, 274 (1966). ⁿ W. H. Zachariasen, *ibid.*, **17**, 749 (1964). ^o M. Marezio and P. Remick, *J. Chem. Phys.*, **44**, 3348 (1966). ^p M. Marezio, H. A. Plettinger, and W. H. Zachariasen, *Acta Crystallogr.*, **16**, 594 (1963). ^q W. H. Zachariasen, *J. Chem. Phys.*, **5**, 919 (1937). ^r M. Marezio and P. D. Dernier, *ibid.*, **25**, 965 (1969). ^s S. Block, A. Perloff, and C. E. Weir, *ibid.*, **17**, 314 (1966). ^t P. D. Dernier, *ibid.*, **25**, 1001 (1969). ^u A. D. Mighell, A. Perloff, and S. Block, *ibid.*, **20**, 819 (1966). ^v S. Block, G. Burley, A. Perloff, and R. D. Mason, *J. Res. Nat. Bur. Stand.*, **62**, 95 (1959). ^w S. V. Berger, *Acta Chem. Scand.*, **3**, 660 (1949). ^{bb} T. Ito, "X-Ray Studies on Polymorphism," Maruzen, Tokyo, 1950, p 143. ^{cc} A. A. Ballman, *Amer. Mineral.*, **47**, 1380 (1962). ^{cd} A. D. Mills, *Inorg. Chem.*, **1**, 960 (1962). ^{ce} G. Blasse and A. Brill, *J. Inorg. Nucl. Chem.*, **29**, 266 (1967).

having a pendant bond (B-O-) is to be counted as part of the motif. Similarly, only two-thirds (or one-third) of each O''' oxygen, represented as having one (or two) pendant bonds, is to be counted as part of the motif.

The boron atoms are of two kinds. Some (B₃) have three oxygen neighbors; the others (B₄) have four. The oxygens are of three categories: those (O') with only one close boron, those (O'') which bridge between two borons, and those (O''') which have three close boron atoms. The last type has been found in a high-pressure form of B₂O₃ and in two anhydrous borates: SrB₄O₇ and PbB₄O₇.

The nonbridging oxygens (O') always and the bridging oxygens (O'') usually have, in addition, one or more cation neighbors.

The strongest bonding is between boron and oxygen atoms and for many purposes the cation-to-oxygen bonding can be neglected. Doing this brings to light some interesting and important regularities. Neglecting the cations and their contacts, the only boron and oxygen structon types observed are those in Tables III and IV.

The absence of B₄ atoms with O' neighbors is not unreasonable, considering the fact that both B₄ and O' have formal charges of 1-. (Formal charges are calculated on the arbitrary assumption that each shared electron pair is shared equally between the two atoms it joins.⁸) Of course, the charge on a nonbridging oxygen is partly—but only partly—compensated by the cations that are invariably close to it. The author assumes that, under ordinary conditions, B₄ and O' atoms cannot (stably) be close neighbors.

The fact that O''' atoms have only been found when surrounded by B₄ atoms is similarly explained. An O''' atom, with a formal charge of 1+, is stabilized by being attached to three negatively charged B₄ atoms. The author assumes that, at least under ordinary conditions, B₃ and O''' atoms cannot (stably) be close neighbors.

Although compositions containing more than one type of B₃ structon or more than one type of B₄ structon (neglecting cations) are surely common in liquids and glasses, only a few are found among the known structures of crystalline borates. In two of these (the isostructural SrB₄O₇ and PbB₄O₇) the two boron structon types (B₄(2O'', 2O''')) and (B₄(3O'', O''')) are adjacent in Table III. This is similar to the usual situation in silicate crystals.³ In the other two examples (the isostructural high-pressure phases III of CaB₂O₄ and SrB₂O₄) the two boron structon types (B₃(2O', O'')) and (B₃(3O')) are not adjacent in Table III. This exception to the usual rule can be attributed to geometrical factors and the requirement for three-dimensional periodicity of a small motif.

Table I shows many examples of coexistence of two types (neglecting cations) of O'' structons. In only one case (BaB₄O₇), however, do two types coexist that are not adjacent in Table IV.

Nonbridging oxygens have not been found in any of the compounds with relatively small amounts of the

(8) M. L. Huggins, *Chem. Rev.*, **10**, 437 (1932).

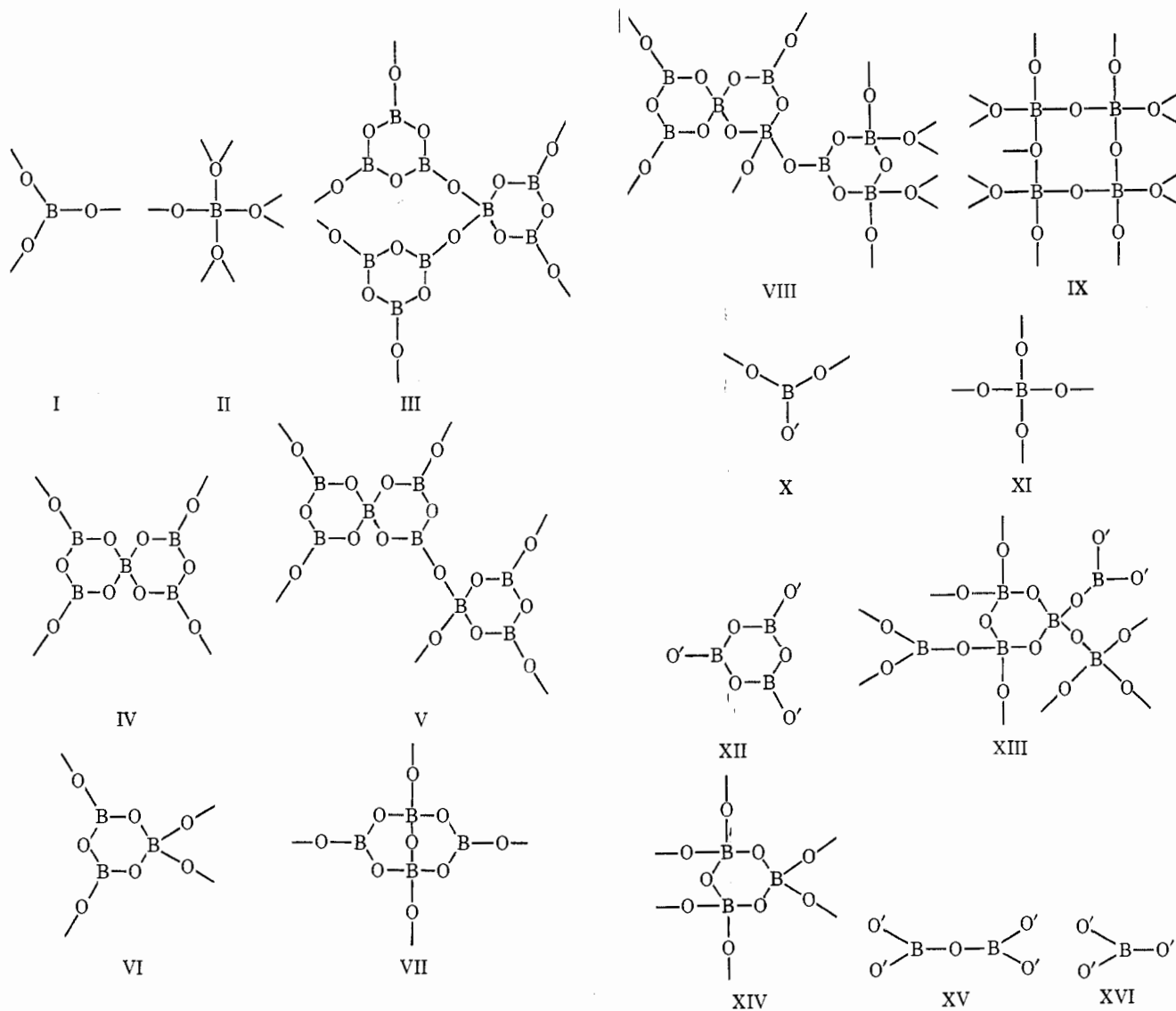
TABLE II
MOTIFS

TABLE III

BORON STRUCTON TYPES

 $\langle B_3(3O'') \rangle$, $\langle B_3(O', 2O'') \rangle$, $\langle B_3(2O', O'') \rangle$, $\langle B_3(3O') \rangle$ $\langle B_4(4O'') \rangle$ $\langle B_4(O'', 3O'') \rangle$, $\langle B_4(2O'', 2O'') \rangle$, $\langle B_4(3O'', O'') \rangle$

TABLE IV

OXYGEN STRUCTON TYPES, NEGLECTING CATIONS

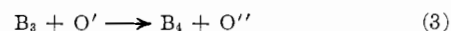
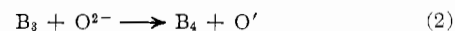
 $\langle O'(B_3) \rangle$ $\langle O''(2B_3) \rangle$, $\langle O''(B_3, B_4) \rangle$, $\langle O''(2B_4) \rangle$ $\langle O'''(3B_4) \rangle$

component oxide other than boric oxide—specifically, with ρ equal to or less than 0.50 (or σ equal to or less than 1.75). Apparently, O' and B_3 cannot exist stably together except when the ratio of metal ions to oxygen is large. Let us consider why this is so.

Boric oxide, in the crystal phase stable at ordinary temperatures and pressures and also in the glass,⁹ contains only structons of the types $\langle B_3(3O'') \rangle$ and $\langle O''-$

(9) B. E. Warren, Lecture at the Symposium Honoring Sir Lawrence Bragg, London, April 1-3, 1970.

$(2B_3) \rangle$. On addition of an alkali or other oxide, composed of cations and oxide ions, changes represented by the following simplified equations occur



Judging from the observed structures, reaction 2 always goes completely, also (nearly always, under normal conditions of crystal formation) reaction 4. The extent to which reaction 3 takes place, however, depends greatly on the relative numbers of oxygens of the two types and the cations, the "effective charges" on the oxygens, and the charges and coordination number requirements and limitations of the cations. Geometrical limitations also play a role, especially in crystals.

Numerical values for the effective charges on the oxygens can be calculated as follows.⁴ Starting with a charge of 2- units for the oxygen, add 1+ unit for each three-coordinated boron, $3/4+$ unit for each four-

coordinated boron, and $\nu/z+$ units for each cation neighbor. Here ν is the charge on the cation and z is its coordination number.

This procedure is essentially that used by Pauling¹⁰ in applying his "electrostatic valence rule" and by Zachariassen,¹¹ Marezio, Remeika, and Dernier,¹² and others in "valence balancing." The effective charge, calculated in this manner, is a rough measure of the departure from local neutrality and so of the instability of the local structure with regard to coulombic forces. Marezio, *et al.*, went a step further in correcting the contributions of the contacts for departures of the interatomic distances from the normal ones. Although this useful correction has not been applied here, it may be noted that in general relatively large negative values of the effective charge on an oxygen result in short cation-to-oxygen distances and relatively large positive values of the effective charge result in long distances. Conversely, more accurate effective charges could be calculated by increasing the contributions of relatively close neighbors and decreasing those of more distant neighbors.

Another source of inaccuracy in the calculation of effective charges results from the indefiniteness, in many cases, of the coordination number of the cation. If, in addition to the oxygens at close distances, there are others at various intermediate distances, all that contribute significantly to the total attraction energy should be considered (but with unequal contributions) in calculating the "true" effective charges. Nevertheless, the present less accurate, but much simpler, procedure is useful.

The effective charges (c_0), calculated as described, are given as subscripts to the formulas for the oxygen structons in Table I.

The algebraic sum of the effective charges on all the oxygens is zero. The sum of their magnitudes is a rough measure of the departure of the cation-oxygen contact distribution from a hypothetical most stable distribution giving no excess charge at each atom.

In making contacts with oxygens, a cation would be expected to show preference for the oxygens having the most negative value of c_0 , calculated without considering the cations. The preference should then decrease in the order: $\langle O'(B_4) \rangle_{1.25-}$, $\langle O'(B_3) \rangle_{1-}$, $\langle O''(2B_4) \rangle_{0.5-}$, $\langle O''(B_3, B_4) \rangle_{0.25-}$, $\langle O''(2B_3) \rangle_0$, $\langle O''(3B_4) \rangle_{0.25+}$. The c_0 values are here given as subscripts, as in Table I.

The preferences are of course modified if the oxygens make contact with other cations. Careful study of the observed structon types (Table I) shows general agreement with these expectations. Geometric and other factors prevent perfect agreement.

The coordination numbers chosen, on the basis of the X-ray data, for the cations in the borate crystals are collected in Table V.

Disregarding the high-temperature and high-pressure

TABLE V
COORDINATION NUMBERS OF CATIONS^a

Li (4), 5		
Na 7, 8	Mg 6	Al 6
K 7	Ca 8, (10), (12)	Ga 6
Rb 7	Sr 8, 9, (10), (12)	Cr 6
Cs 10	Ba (6), 9, 10	Ln 6
Ag 7, 8	Cd 7	
	Co 6	

^a The numbers in parentheses have been observed only in unstable phases.

phases, the observed types of oxygen structons, not neglecting the cations, are those listed in Table VI. The

TABLE VI
OXYGEN STRUCTON TYPES, NOT NEGLECTING CATIONS

$\langle O'(B_3, 2M_{II}) \rangle$, $\langle O'(B_3, 2M_{III}) \rangle$, $\langle O'(B_3, 3M_{II}) \rangle$, $\langle O'(B_3, 4M_{II}) \rangle$,
 $\langle O'(B_3, 5M_{II}) \rangle$
 $\langle O''(2B_3) \rangle$, $\langle O''(2B_3, M_I) \rangle$, $\langle O''(2B_3, M_{II}) \rangle$, $\langle O''(2B_3, 2M_I) \rangle$
 $\langle O''(B_3, B_4, M_I) \rangle$, $\langle O''(B_3, B_4, M_{II}) \rangle$, $\langle O''(B_3, B_4, 2M_I) \rangle$,
 $\langle O''(B_3, B_4, 2M_{II}) \rangle$
 $\langle O''(2B_4, M_{II}) \rangle$, $\langle O''(2B_4, 2M_{II}) \rangle$
 $\langle O'''(3B_4) \rangle$

metal cations are here classified (M_I , M_{II} , M_{III}) on the basis of their charges.

Examination of Table I shows that, in the stable phases, c_0 only rarely has a magnitude greater than 0.25. The largest calculated c_0 is 0.33— for $\langle O'(B_3, 2M_{II}) \rangle$ in $Mg_2B_2O_5$.

The high-temperature and high-pressure phases tend to have structons with more contacts than the phases stable at normal temperatures and pressures, even though their c_0 values depart more from zero. Examples are found in $B_2O_3(II)$, $CaB_2O_4(III$ and $IV)$, and $SrB_2O_4(III$ and $IV)$.

Structon Sets

Neglecting the cations, the structons in the borate crystals having ρ less than $1/2$ are the following: $\langle B_3(3O'') \rangle$, $\langle B_4(4O'') \rangle$, $\langle O''(2B_3) \rangle$, and $\langle O''(B_3, B_4) \rangle$. These constitute a "minimum set."

For this and other minimum sets, the numbers of each structon type, per boron atom, are easily calculated as functions of the overall composition, *e.g.*, in terms of ρ or σ . The results of such calculations are given, for this and some other minimum sets pertinent to the compounds in Table I and the present discussion, in Table VII.

For each minimum set the range over which the concentrations of all the structon types are positive is given. Set 2, for example, cannot exist for ρ values higher than $3/7$, the concentration at which the number of $\langle O''(2B_3) \rangle$ structons becomes zero. With higher ρ values (larger proportions of the oxide or oxides other than B_2O_3) there must either be some $\langle O''(2B_4) \rangle$ structons or some nonbridging oxygen atoms, presumably present as $\langle O'(B_3) \rangle$ or both. (See Table IV and the discussion immediately following it.)

If, in the range between $\rho = 3/7$ and $\rho = 1$, $\langle O''(2B_4) \rangle$ structons, but no nonbridging oxygens, were present, the minimum structon set (neglecting cations) would

(10) L. Pauling, *J. Amer. Chem. Soc.*, **51**, 1010 (1929).

(11) W. H. Zachariassen, *Acta Crystallogr.*, **16**, 385 (1963).

(12) M. Marezio, J. P. Remeika, and P. D. Dernier, *ibid.*, Sect. B, **25**, 965 (1969).

TABLE VII
MINIMUM STRUCTON SETS, NEGLECTING CATIONS

Set	ρ	Structons
Class A. All O Atoms Bridging between Borons		
1	0	$1\langle B_3(3O'') \rangle, \frac{3}{2}\langle O''(2B_3) \rangle$
2	0-0.4286	$(1 - \rho)\langle B_3(3O'') \rangle, \rho\langle B_4(4O'') \rangle, (\frac{3}{2} - 7\rho/2)\langle O''(2B_3) \rangle, 4\rho\langle O''(B_3, B_4) \rangle$
3	0.4286	$\frac{4}{7}\langle B_3(3O'') \rangle, \frac{3}{7}\langle B_4(4O'') \rangle, \frac{12}{7}\langle O''(B_3, B_4) \rangle$
4	0.4286-1	$(1 - \rho)\langle B_3(3O'') \rangle, \rho\langle B_4(4O'') \rangle, (3 - 3\rho)\langle O''(B_3, B_4) \rangle, (7\rho/2 - \frac{3}{2})\langle O''(2B_4) \rangle$
5	1	$1\langle B_4(4O'') \rangle, 2\langle O''(2B_4) \rangle$
Class B. All B Atoms Tribonded to Oxygens		
1	<i>a</i>	<i>a</i>
6	0-1	$(1 - \rho)\langle B_3(3O'') \rangle, \rho\langle B_3(O', 2O'') \rangle, (\frac{3}{2} - \rho/2)\langle O''(2B_3) \rangle, \rho\langle O'(B_3) \rangle$
7	1	$1\langle B_3(O', 2O'') \rangle, 1\langle O''(2B_3) \rangle, 1\langle O'(B_3) \rangle$
8	1-2	$(2 - \rho)\langle B_3(O', 2O'') \rangle, (\rho - 1)\langle B_3(2O'', O'') \rangle, (\frac{3}{2} - \rho/2)\langle O''(2B_3) \rangle, \rho\langle O'(B_3) \rangle$
9	2	$1\langle B_3(2O', O'') \rangle, \frac{1}{2}\langle O''(2B_3) \rangle, 2\langle O'(B_3) \rangle$
10	2-3	$(3 - 2\rho)\langle B_3(2O', O'') \rangle, (\rho - 2)\langle B_3(3O'') \rangle, (\frac{3}{2} - \rho/2)\langle O''(2B_3) \rangle, \rho\langle O'(B_3) \rangle$
11	3	$1\langle B_3(3O'') \rangle, 3\langle O'(B_3) \rangle$
Class C. Containing Some Oxygens Tribonded to Borons		
12	0	$1\langle B_4(O'', 3O'') \rangle, \frac{1}{2}\langle O''(2B_4) \rangle, 1\langle O'''(3B_4) \rangle$
13	0-0.3333	$3\rho\langle B_4(2O'', 2O'') \rangle, (1 - 3\rho)\langle B_4(O'', 3O'') \rangle, (\frac{1}{2} + 3\rho/2)\langle O''(2B_4) \rangle, (1 - \rho)\langle O'''(3B_4) \rangle$
14	0.3333	$1\langle B_4(2O'', 2O'') \rangle, 1\langle O''(2B_4) \rangle, \frac{2}{3}\langle O'''(3B_4) \rangle$
15	0.3333-0.6667	$(3\rho - 1)\langle B_4(3O'', O'') \rangle, (2 - 3\rho)\langle B_4(2O'', 2O'') \rangle, (\frac{1}{2} - 3\rho/2)\langle O''(2B_4) \rangle, (1 - \rho)\langle O'''(3B_4) \rangle$
16	0.6667	$1\langle B_4(3O'', O'') \rangle, \frac{3}{2}\langle O''(2B_4) \rangle, \frac{1}{3}\langle O'''(3B_4) \rangle$
17	0.6667-1	$(3\rho - 2)\langle B_4(4O'') \rangle, (3 - 3\rho)\langle B_4(3O'', O'') \rangle, (\frac{1}{2} + 3\rho/2)\langle O''(2B_4) \rangle, (1 - \rho)\langle O'''(3B_4) \rangle$
5	<i>a</i>	<i>a</i>
Class D. Containing Both Three- and Four-Coordinated Borons and Both Bridging and Nonbridging Oxygens		
18	0.4286-1	$(1 - \rho)\langle B_3(3O'') \rangle, (7\rho/6 - \frac{1}{2})\langle B_3(O', 2O'') \rangle, (\frac{1}{2} - \rho/6)\langle B_4(4O'') \rangle, (7\rho/6 - \frac{1}{2})\langle O'(B_3) \rangle, (2 - 2\rho/3)\langle O''(B_3, B_4) \rangle$
19	1	$\frac{2}{3}\langle B_3(O', 2O'') \rangle, \frac{1}{3}\langle B_4(4O'') \rangle, \frac{2}{3}\langle O'(B_3) \rangle, \frac{4}{3}\langle O''(B_3, B_4) \rangle$
20	1-1.800	$(\frac{3}{2} - 5\rho/6)\langle B_3(O', 2O'') \rangle, (\rho - 1)\langle B_3(2O', O'') \rangle, (\frac{1}{2} - \rho/6)\langle B_4(4O'') \rangle, (7\rho/6 - \frac{1}{2})\langle O'(B_3) \rangle, (2 - 2\rho/3)\langle O''(B_3, B_4) \rangle$
21	1.800	$\frac{4}{5}\langle B_3(2O', O'') \rangle, \frac{1}{5}\langle B_4(4O'') \rangle, \frac{3}{5}\langle O'(B_3) \rangle, \frac{4}{5}\langle O''(B_3, B_4) \rangle$
22	1.800-3	$(2 - 2\rho/3)\langle B_3(2O', O'') \rangle, (5\rho/6 - \frac{3}{2})\langle B_3(3O'') \rangle, (\frac{1}{2} - \rho/6)\langle B_4(4O'') \rangle, (7\rho/6 - \frac{1}{2})\langle O'(B_3) \rangle, (2 - 2\rho/3)\langle O''(B_3, B_4) \rangle$

^a As above.

be set 4. At the limit $\rho = 1$ only the structons of set 5 would remain. Actually, $Li_2B_2O_7$ and CdB_4O_7 , having $\rho = \frac{1}{2}$, have set 4, with equal numbers of $\langle B_3(3O'') \rangle$ and $\langle B_4(4O'') \rangle$ structons. BaB_4O_7 also has all oxygens bridging, but, as an exception to the usual rule, its structons do not conform to a minimum set. It contains bridging oxygens of all three types: $\langle O''(2B_3) \rangle$, $\langle O''(B_3, B_4) \rangle$, $\langle O''(2B_4) \rangle$. Reaction 4 has not taken place completely.

There are several crystals of known structure with $\rho = 1$. Metastable phases of $LiBO_2$, CaB_2O_4 , and SrB_2O_4 have structon set 5. The others and also the known borates with $\rho = 2$ and 3 all contain nonbridging oxygens.

It may be noted that nuclear magnetic resonance studies on alkali borate glasses having ρ greater than $\frac{3}{7}$ show fractions of boron atoms that are four-coordinated that can only be explained by assuming that, as M_2O is added, reaction 3 takes place to some extent but not completely. The compositions do not conform to any minimum set of structons, but to a mixture of two minimum sets (sets 4 and 18, for $\frac{3}{7} < \rho < 1$). Discussion of the equilibria involved and deduction of structon types and their relative numbers as functions of the composition will be left for another paper, dealing specifically with borate glasses. For present purposes it need only be noted that it has been possible to obtain crystals for only a few very special compositions, for which the numbers of structon types required to be present are relatively low. The structons present in a crystal must not only be able to satisfy well the interatomic forces, but they must permit efficient packing and a simple repeating unit. In some cases temperature and pressure effects are also important.

To illustrate this point, it may be noted that, when $\rho = 1$, the fraction of boron that is four-coordinated is usually zero in the more stable crystal phases; it is $\frac{2}{3}$ or 1 in some metastable phases, and it is approximately $\frac{1}{3}$ in alkali borate glasses. The structons in the glasses doubtless conform more closely to the equilibrium distribution than do those in the crystals.

Oxygens with Three Boron Neighbors

We shall now consider the stability of structon sets containing oxygen atoms (O'') with three boron neighbors, as compared with other structon sets for the same overall compositions. To make the problem definite and simple, structon sets containing nonbridging oxygen atoms (O') will not be dealt with here; the comparison will be between sets of class A and sets of class C. (All other known crystal structures having the same or nearly the same composition as those which contain O''' atoms contain O'' but no O' atoms.) Also, the only borates considered will be those with bivalent metal cations, having a coordination number of 9.

The problem will be divided into two parts: (1) a comparison of the relative stabilities of the cation-oxygen interactions and (2) a comparison of the relative energies of the boron-oxygen interactions.

With regard to (1), it seems reasonable to assume that, other things being equal, the most stable structure will be that having the lowest sum of the magnitudes of the effective charges on the oxygen atoms, calculated as already described.

The effective charge sums for class A and class C structon sets, for a series of ρ values, are listed in Table VIII, with the differences between the sums for the two sets. The quantities not enclosed in parentheses are minimum values for any structon set containing only structon types (Tables III and VI) observed in stable crystals, excluding high-temperature and high-pressure phases. The sums enclosed in parentheses are for sets which contain the structon type $\langle O''(2B_4, 3M) \rangle$.

From column 6, giving the differences between the

TABLE VIII
EFFECTIVE CHARGE SUMS AND FRACTIONS OF BORON ATOMS
THAT ARE TETRAHEDRALLY COORDINATED, FOR STRUCTON SETS A AND C^a

ρ	Class A sets		Class C sets		Differences	
	$\Sigma c_0 $	B_4	$\Sigma c_0 $	B_4	$\Delta\Sigma c_0 $	ΔB_4
0	0	0	0.500	1	0.500	1.000
0.111	0.022	0.111	0.444	1	0.422	0.889
0.200	0.039	0.200	0.400	1	0.361	0.800
0.250	0.049	0.250	0.375	1	0.326	0.750
0.429	0.083	0.429	0.286	1	0.203	0.571
0.500	(0.083), 0.097	0.500	0.250	1	0.153, (0.167)	0.500
0.667	(0.111), 0.130	0.667	0.167	1	0.037, (0.056)	0.333
0.750	(0.125), 0.146	0.750	(0.167)	1	(0.042)	0.250
0.800	(0.133), 0.156	0.800	(0.167)	1	(0.033)	0.200
0.900	(0.144)	0.900	(0.167)	1	(0.023)	0.100

^a The effective charge sums in parentheses are for structon sets that include $\langle O''(2B_4, 3M) \rangle$. Otherwise, the only oxygen structon types are those in Table VI.

effective charge sums for the two classes, one can conclude that, if the assumptions underlying the calculations were correct and if no other factors were involved, the class A sets (containing no O''') should be more stable than the class C sets (containing O''') over the whole range of composition for which these sets are valid, but that the difference in stability decreases as ρ increases, reaching a moderately low value at $\rho = 1/2$ and a very low value at $\rho = 2/3$. When ρ is greater than $2/3$, class C structures are only possible if the structon type $\langle O''(2B_4, 3M) \rangle$ is allowable. This type has not been observed in stable crystal phases of known structure; it may require too much crowding of electro-positive atoms around the oxygen in question.

At ρ equal to $1/2$, crystals with three different types of structure have been studied: CdB_4O_7 , with $z = 7$, has a class A set of structons; BaB_4O_7 , with some Ba cations having a coordination number of 9 and some having a coordination number of 10, has a structure, not conforming to any minimum set, that (like that of CdB_4O_7) contains no O''' ; SrB_4O_7 and PbB_4O_7 , with coordination numbers of 8, have a structure of the class C type, containing O''' .

Calculations of $\Sigma|c_0|$ (for $\rho = 1/2$) for a class A structure with $z = 7$ or 8 and for a structure like that of BaB_4O_7 , except for a coordination number (for all the cations) of 9, lead to results differing only slightly from those given in column 2 of the table.

Calculations of $\Sigma|c_0|$ for borates of alkali and other M_I cations lead to results very similar to those for M_{II} borates, except that the class C structures require $\langle O''(2B_4, 3M) \rangle$ structons for ρ larger than $1/6$ and $\langle O''(2B_4, 4M) \rangle$ structons for ρ larger than $1/3$. Since, for low values of ρ , $\Sigma|c_0|$ for class C is always much higher than for class A, it seems unlikely that any crystalline M_I borates will be found to have class C structures.

The boron atoms in class C sets all have four close oxygen neighbors. In the class A sets some have three and some have four oxygen neighbors. If these atoms were all ions, if the oxygen-to-oxygen repulsions could be neglected, and if the B-O distances were all equal, the ratio of the boron-to-oxygen attraction energy for each B_4 boron to that for each B_3 boron would be $4/3$. Of course these provisos are not valid, but, on the average, the magnitude of the attraction energy between a

boron and the oxygens surrounding it would be expected to be somewhat greater for a B_4 boron than for a B_3 boron. Other things being equal, then, the larger the fraction of tetrahedral boron atoms in the structure, the greater should be the stability. This fraction is given in the columns headed B_4 in Table VIII. From the differences between the values for class A and class C structures (see column 7), one sees that the boron-oxygen interaction energy contributions favor the class C structures at all values of ρ but decreasingly as ρ increases. At ρ equal to $1/2$, for which the borates of Sr and Pb are known to have a class C structure, B_4 is $1/2$. This is apparently enough to overcome the small positive value of $\Delta\Sigma|c_0|$, favoring a class A structure. For $\rho \leq 1/4$, the boron-oxygen contribution to the stability is apparently insufficient to outweigh the cation-oxygen contribution, measured by $\Sigma|c_0|$. For ρ between $1/2$ and $2/3$, $\Delta\Sigma|c_0|$ is very low and ΔB_4 is still between $1/2$ and $1/3$. It seems likely that a glass or a glass melt at a temperature just above that at which it solidifies would contain considerable amounts of O''' . If any stable crystal phase can be obtained in this composition region, it is likely to have either a class C structure or one containing some O' oxygens.

For ρ values between $2/3$ and 1, a class C crystal structure cannot exist without $\langle O''(2B_4, 3M) \rangle$ structons. How stable or unstable these are is at present unknown. If not very unstable relative to alternative types, crystalline compounds in this range, if they can be obtained, might have class C structures, containing O''' . They might, however, have structures containing O' , which have not been considered in the foregoing comparisons. Class C structon sets cannot exist for $\rho \geq 1$.

The effect of the density of packing of the atoms in the structure has, up to now, been neglected. Increasing the number of close neighbors around an atom increases the density of packing (even after allowing for the slight change in interatomic distance). Class C structures, with all B_4 borons and some O''' oxygens, thus have higher densities, if other structural factors are the same, than class A structures of the same overall compositions. Changing the density changes the interaction energy between nonclosest-neighbor atoms. Except in very unusual cases, the van der Waals interactions between nonclosest neighbors are all attractions,

increasing as the interatomic distances decrease, hence, as the density increases. The coulombic energies between nonclosest neighbors would be expected to be fairly large in substances such as the borates. They are both attractions and repulsions, and both types increase as the density increases. It seems impossible to evaluate the net effect in any simple way and it will not now be attempted.

Neglecting the possible effect of differences in the density dependence of the nonclosest-neighbor coulombic energy, increasing pressure should favor class C structures, with higher coordination numbers and higher densities, over class A structures of the same chemical composition. This is in line with the fact that the stable structure for boric oxide at normal pressures is class A, while a high-pressure phase has a class C structure.

Conclusion

The types of structons in known structures of anhydrous boric oxide and borates have been listed and compared. Certain regularities have been noted and related to stability factors. It has been found that the arrangements of boron and oxygen atoms almost invariably conform to a few "minimum sets" of structon types. The relative stabilities of different sets, as affected by overall composition and by the cation-oxygen arrangements, have been discussed in some detail. Factors affecting the stability of nonbridging oxygens (O') and oxygens with three boron neighbors (O''') have been especially considered. It is hoped that this paper will serve as a basis for prediction of the structon types (and relative numbers of each) in crystals that have not yet been analyzed and in borate glasses.

CONTRIBUTION FROM THE TODD WEHR CHEMISTRY BUILDING,
MARQUETTE UNIVERSITY, MILWAUKEE, WISCONSIN 53233

Metal Isotope Effect on Metal-Ligand Vibrations.

VI. Metal Complexes of 8-Hydroxyquinoline¹

BY NOBORU OHKAKU AND KAZUO NAKAMOTO*

Received August 3, 1970

Low-frequency infrared spectra ($650\text{--}100\text{ cm}^{-1}$) have been obtained for isotopic pairs of some first-row transition metal oxinates (8-hydroxyquinolinates) of the types MQ_2 ($\text{M} = {}^{58,62}\text{Ni}$, ${}^{63,65}\text{Cu}$, and ${}^{64,66}\text{Zn}$), $\text{MQ}_2 \cdot 2\text{H}_2\text{O}$ ($\text{M} = {}^{54,57}\text{Fe}$, ${}^{58,62}\text{Ni}$, and ${}^{64,66}\text{Zn}$), $\text{CuQ}_2 \cdot 2\text{H}_2\text{O}$ – $\text{CuQ}_2 \cdot 2\text{D}_2\text{O}$, and MQ_3 ($\text{M} = {}^{54,57}\text{Fe}$) where Q denotes an oxinate anion. Based on the observed isotopic shifts, the metal-oxygen and metal-nitrogen stretching bands have been assigned in the regions of $332\text{--}210$ and $300\text{--}190\text{ cm}^{-1}$, respectively. Structures of several metal oxinates have been elucidated from the number of isotope-sensitive bands and the general pattern of the spectra. The spectra of CoQ_2 and its dihydrated derivative have been studied. The spectra of α and β forms of anhydrous CuQ_2 have been compared and discussed.

Introduction

The importance of metal oxinates (8-hydroxyquinolinates) in analytical chemistry is well known.² The oxine ligand plays an important role in some biological systems, and its function is related at least in part to its chelating ability with metals.³ Thus far, metal oxinates have been a subject of various physicochemical investigations including X-ray diffraction,^{4–10} ir,^{11–15}

uv-visible,^{16–18} nmr,¹⁹ magnetic susceptibility,²⁰ mass spectrometry,²¹ esr,²² ENDOR (electron nuclear double resonance),²³ and potentiometric studies.²⁴

X-Ray diffraction studies have been made on a series of compounds of the type $\text{MQ}_2 \cdot 2\text{H}_2\text{O}$, where M is Zn, Cu, Ni, Co, Cd, or Pb, and Q is an oxinate anion. The results of these investigations^{4–6} show that two chelating oxinate anions coordinate to the metal by forming a trans-planar structure, and two water molecules occupy the axial positions to complete a six-coordinate

(1) This work was supported by an ACS-PRF unrestricted research grant (3318-3.5).

(2) (a) F. J. Welcher, "Organic Analytical Reagents," Van Nostrand, New York, N. Y., 1947; (b) I. M. Kolthoff and F. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed, Macmillan, New York, N. Y., 1952, pp 88–90.

(3) S. Chaberek and A. E. Martell, "Organic Sequestering Agents," Wiley, New York, N. Y., 1959.

(4) (a) L. L. Merritt, *Anal. Chem.*, **25**, 718 (1953); (b) L. L. Merritt, R. T. Cady, and B. W. Mundy, *Acta Crystallogr.*, **7**, 473 (1954).

(5) R. Kruh and C. W. Diggins, *J. Amer. Chem. Soc.*, **77**, 806 (1955).

(6) G. J. Palenik, *Acta Crystallogr.*, **17**, 696 (1964).

(7) R. C. Hoy and R. H. Morriss, *ibid.*, **22**, 476 (1967).

(8) F. Kanakubo, K. Ogawa, and I. Nitta, *Bull. Chem. Soc. Jap.*, **36**, 422 (1963).

(9) G. J. Palenik, *Acta Crystallogr.*, **17**, 687 (1964).

(10) C. K. Prout and A. G. Wheeler, *J. Chem. Soc. A*, 1286 (1966).

(11) K. G. Stone, *J. Amer. Chem. Soc.*, **76**, 4997 (1954).

(12) R. G. Charles, H. Freiser, R. Friedel, L. E. Hilliard, and W. D. Johnson, *Spectrochim. Acta*, **8**, 1 (1956).

(13) J. E. Tackett and D. T. Sawyer, *Inorg. Chem.*, **3**, 692 (1964).

(14) (a) R. J. Magee and L. Gordon, *Talanta*, **10**, 851 (1963); (b) *ibid.*, **10**, 961 (1963); (c) *ibid.*, **10**, 967 (1963).

(15) R. Larsson and O. Eskilsson, *Acta Chem. Scand.*, **22**, 1067 (1968).

(16) K. Sone, *J. Amer. Chem. Soc.*, **75**, 5207 (1953).

(17) L. Morpurgo and R. J. P. Williams, *J. Chem. Soc. A*, 73 (1966).

(18) S. G. Schulman, W. P. Kilroy, and H. Gershon, *J. Phys. Chem.*, **72**, 3372 (1968).

(19) B. C. Baker and D. T. Sawyer, *Anal. Chem.*, **40**, 1945 (1968).

(20) W. Matoush and F. Basolo, *J. Amer. Chem. Soc.*, **75**, 5663 (1953).

(21) A. E. Jenkins, J. R. Majer, and M. J. A. Reade, *Talanta*, **14**, 1213 (1967).

(22) H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962).

(23) G. H. Rist and J. S. Hyde, *ibid.*, **50**, 4532 (1969).

(24) (a) W. D. Johnston and H. Freiser, *J. Amer. Chem. Soc.*, **74**, 5239 (1952); (b) H. Irving and H. S. Rossotti, *J. Chem. Soc.*, 2916 (1954); (c) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, New York, N. Y., 1952, pp 184, 556.