in both ions the central atom possesses a lone valence electron pair, the size of bromine permits only a maximum coordination number of 6 (toward fluorine) and the lone pair in BrF_6^- is sterically inactive and centrosymmetric. In IF_6^-, the larger central atom can readily accept seven or eight ligands, as demonstrated by the existence of IF_7 and IF_8^-,[17,18] and, therefore, the lone valence electron pair becomes sterically active and acts as a ligand. On the assumption of a similar ease of delocalization of the free valence electron pair in trigonal-bipyramidal arrangements, a free valence electron pair can then be expected to possess little directional repulsive selectivity and to compress preferentially the most compressible bond angle. In an idealized SF_4 structure, the 120° equatorial FSF angle obviously should be compressed more easily than the 90° angles formed between the axial ligands and the fluorine containing equatorial plane.

On the other hand, the π orbitals of an S=X double bond are more localized and concentrated between the sulfur and the X atom in the equatorial and the axial planes of the molecule. Depending on the relative population of these orbitals, preferential repulsion of either the axial or the equatorial fluorines is possible. Thus, the "shape" of the S=X π bond is responsible for the preferred direction of the repulsion effect and must be considered when the structure of an unknown molecule is predicted.

In view of these directional repulsion effects, the change in a single bond angle is not a good measure for the overall repulsive strength of a ligand or a free valence electron pair. Since the repulsion of all the other ligands must be considered, the average quadruple angle[10] should be used for such a comparison. In SF_4, OSF_4, and H_2CSF_4, these average quadruple angles are 111.5, 110.3, and 113.3°, respectively, indicating that the overall repulsive strengths of a free valence electron pair and of a S=X π bond are, within experimental error, quite similar but that they strongly differ in their directions.

Since the molecular structure of SF_4O has not yet been established beyond doubt (four models have been proposed on the basis of an electron diffraction study)[5] and since one might argue that secondary effects such as the difference in the oxidation state of the sulfur central atom might be of importance, the structural study of a trigonal-bipyramidal molecule containing both a lone valence electron pair and a doubly bonded oxygen atom was important. Such a molecule is ClF_3O, the structure of which was recently established:[11]

side view   top view
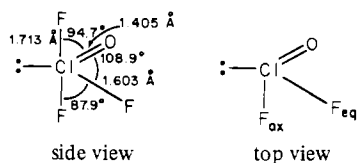
The fact that the axial fluorine atoms are repelled more strongly by the oxygen ligand than by the lone pair confirms the existence of directional repulsion effects in trigonal-bipyramidal molecules and supports the conclusions reached from the comparison of the SF_4, OSF_4, H_2CSF_4 series.

In summary, in trigonal-bipyramidal molecules, cylindrically nonsymmetric valence electron pairs can result in directional repulsion effects. These effects can be rather pronounced and cannot be accounted for by simple VSEPR theory.[1,2]

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Bonding in Metal Borohydride Complexes

Sir:

The borohydride ligand has been shown in various structural studies to bond to a wide variety of metal ions via bidentate,[1-23] tridendate,[10,16,21-31] and (in one instance) monodentate hy-

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Table I. Compounds with Metal-Boron Bidentate Hydrogen Bridges

compd	M^{z+} CN	M^{z+} IR^a	M-B, Å	BH_4^- IR^b	ref	comments^c
$Be(BH_4)_2$	6	0.45	1.918 (4)	1.47	1	RT, X-ray, crys
$Be(BH_4)_2$	6	0.45	2.001 (4) (db)^d	1.55	1	RT, X-ray, crys
$[(CH_3)_3CO]Be_3(BH_4)_2$	4	0.27	1.93 (1)	1.66	2	RT, X-ray, crys
B_2H_6	4	0.11	1.775 (3)	1.67	3	25 °C, ED, gas
B_2H_6	4	0.11	1.776 (10)	1.67	4	-190 °C, X-ray, crys
$Al(BH_4)_3$	6	0.535	2.143 (3)	1.61	5	20 °C, ED, gas
$Al(BH_4)_3 \cdot NH_3$	7	0.58	2.229 (8)	1.65	6	RT, X-ray, crys
$Al(BH_4)_3N(CH_3)_3$	7	0.58	2.24 (1)	1.66	7	-160 °C, X-ray, crys
$Al(BH_4)_3N(CH_3)_3$	7	0.58	2.19 (2)	1.61	7	25 °C, X-ray, crys
$[Al(BH_4)_2N(CH_2)_2]_2$	6	0.535	2.19 (1)	1.66	8	RT, X-ray, crys
$Al(BH_4)(CH_3)_2$	4	0.39	2.128 (8)	1.74	9	RT, ED, gas
$Sc(BH_4)_3(OC_4H_8)_2$	10	0.95	2.551 (5)	1.60	10	RT, X-ray, crys
$(C_5H_5)_2Ti(BH_4)$	8	0.76	2.37 (1)	1.61	11	23 °C, X-ray, crys
$(C_5H_5)_2Ti(BH_4)$	8	0.76	2.31 (4)	1.55	12	RT, ED, gas
$Co(p_3)(BH_4)^e$	5	f	2.21 (3)		13	22 °C, X-ray, crys, Co$^+$, high spin d^8
$[CoH(BH_4)[P(C_6H_{11})_3]_2]$	5	0.59	2.13 (1)	1.54	14	RT, X-ray, crys, Co^{2+}, low spin d^7
$[(C_6H_5)_3P]_2Cu(BH_4)$	4	0.64	2.184 (9)	1.54	15	RT, X-ray, crys
$Ga(BH_4)(CH_3)_2$	4	0.47	2.163 (8)	1.69	9	RT, ED, gas
$Y(BH_3)_3(OC_4H_8)_3$	11	1.14	2.68 (2)	1.54	16	23 °C, X-ray, crys
$(C_5H_5)_2Nb(BH_4)$	8	0.81	2.26 (6)	1.45	17	RT, X-ray, crys
$[((C_6H_5)_3P)_2N][Mo(CO)_4BH_4]$	6	f	2.413 (20)		18	RT, X-ray, crys
$MoH(BH_4)(P(CH_3)_3)_4$	6	f	2.468 (12)		19	RT, X-ray, crys
$(CH_3C_5H_4)_2Hf(BH_4)_2$	10	0.89	2.553 (6)	1.66	20	RT, ND, crys
$U(BH_4)_4$	14	1.22	2.86 (4) (db)	1.64	21	RT, ND, crys
$U(BH_4)_4 \cdot O(C_2H_5)_2$	14	1.22	2.89 (1)	1.67	22	21 °C, X-ray, crys
$U(BH_4)_4 \cdot O(CH_3)_2$	14	1.22	2.89 (1)	1.67	22	23 °C, X-ray, crys
$[U(BH_4)_4 \cdot O(n-C_3H_7)_2]_2$	13	1.20	2.90 (4) (db)^g	1.70	23	22 °C, X-ray, crys
$[U(BH_4)_4 \cdot O(n-C_3H_7)_2]_2$	14	1.22	2.84 (5) (db)^g	1.62	23	22 °C, X-ray, crys

^{a} From Shannon^{35} corrected for coordination number; IR = ionic radius in Å. ^{b} Obtained by subtraction of column 3 from column 4.
^{c} Key: RT, room temperature; X-ray, X-ray diffraction; ND, neutron diffraction; ED, electron diffraction; crys, single crystal; gas, gaseous sample. ^{d} All metal bidentate hydrogen boron bridges have two terminal hydrogen atoms unless (db = double bridge) indicated. ^{e} p_3 = 1,1,1-tris((diphenylphosphino)methyl)ethane. ^{f} Ionic radius not available from Shannon. ^{g} Unsymmetrical dimer with one double bridge bidentate borohydride group between the U atoms.
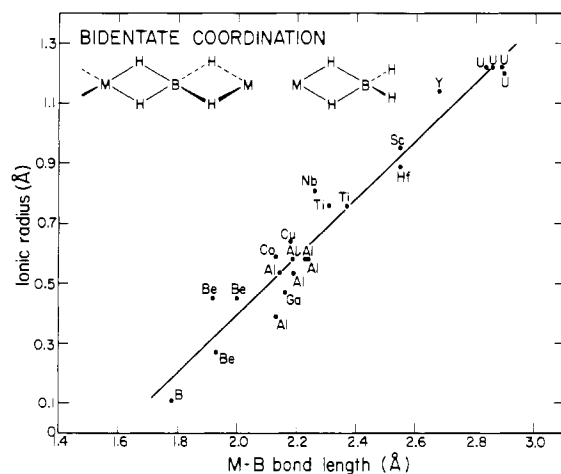

Figure 1. Metal ionic radius vs. M-B bond length for compounds with metal-boron bidentate hydrogen bridges.

Figure 2. Metal ionic radius vs. M-B bond length for compounds with metal-boron tridentate hydrogen bridges.

drogen bridges.^{32} Vibrational spectroscopy also provides data which can be used to determine the metal borohydride coordination geometry in a large number of compounds.^{33,34}
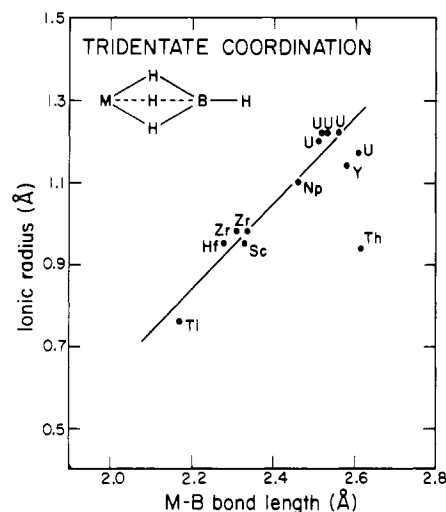
Bernstein et al.,^{21} in their discussion of the neutron diffraction structure of $U(BH_4)_4$, which has both double- and triple-hydrogen-bridged metal-boron bonds, proposed using the metal-boron bond length as a criterion for determining whether the metal ion is bonded by two or three bridging hydrogen atoms to the boron atom. This idea implies one can assign an ionic radius to the borohydride ion. Bernstein et al. determined the values ~ 1.3 and ~ 1.6 Å for the ionic radii of triple-hydrogen-bridge and a double-hydrogen-bridge BH_4^- groups, respectively. Marks and Kolb,^{34} in their review article on metal borohydrides, also tabulated and plotted metal-boron

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Table II. Compounds with Metal-Boron Tridentate Hydrogen Bridges

compd	M^{z+} CN	M^{z+} IR^a	M-B, Å	BH$_4^-$ IR^b	ref	comments^c
Sc(BH$_4$)$_3$(OC$_4$H$_8$)$_2$	10	0.95	2.33 (1)	1.38	10	RT, X-ray, crys
[C$_5$H$_5$TiCl(BH$_4$)]$_2$	8	0.76	2.17 (1)	1.41	24	RT, X-ray, crys
Y(BH$_4$)$_3$(OC$_4$H$_8$)$_3$	11	1.14	2.58 (1)	1.44	16	23 °C, X-ray, crys
Zr(BH$_4$)$_4$	12	0.98	2.308 (10)	1.33	25	RT, ED, gas
Zr(BH$_4$)$_4$	12	0.98	2.34 (3)	1.36	26	-160 °C, X-ray, crys
Hf(BH$_4$)$_4$	12	0.95	2.28 (1)	1.33	27	ND, crys
U(BH$_4$)$_4$	14	1.22	2.52 (1)	1.30	21	RT, ND, crys
Th[N(Si(CH$_3$)$_3$)$_2$]$_3$BH$_4$	6	0.94	2.61 (3)	1.67	28	22 °C, X-ray, crys
(C$_5$H$_5$)$_2$U(BH$_4$)$_2$	12	1.17	2.61 (8)	1.44	29	RT, X-ray, crys
U(BH$_4$)$_4$(OC$_4$H$_8$)$_2$	14	1.22	2.56 (4)	1.34	30	23.5 °C, X-ray, crys
U(BH$_4$)$_4$·O(C$_2$H$_5$)$_2$	14	1.22	2.53 (2)	1.31	22	21 °C, X-ray, crys
U(BH$_4$)$_4$·O(CH$_3$)$_2$	14	1.22	2.53 (2)	1.31	22	23 °C, X-ray, crys
[U(BH$_4$)$_4$·O(n-C$_3$H$_7$)$_2$]$_2$^{d}	13	1.20	2.51 (5)	1.31	23	22 °C, X-ray, crys
[U(BH$_4$)$_4$·O(n-C$_3$H$_7$)$_2$]$_2$^{d}	14	1.22	2.52 (5)	1.30	23	22 °C, X-ray, crys
Np(BH$_4$)$_4$	12	1.10	2.46 (3)	1.36	31	-143 °C, X-ray, crys

^{a} From Shannon[35] corrected for coordination number; IR = ionic radius in Å. ^{b} Obtained by subtraction of column 3 from column 4. ^{c} Key: RT, room temperature; X-ray, X-ray diffraction; ND, neutron diffraction; ED, electron diffraction; crys, single crystal; gas, gaseous sample. ^{d} Unsymmetrical dimer.

distances vs. effective ionic radii for the then available compounds.

Raymond and co-workers[35,36] have recently systematized the structural criteria for ionic bonding in (C$_5$H$_5$)$^-$, (C$_8$H$_8$)$^{2-}$, and N[Si(CH$_3$)$_3$]$_2^-$ metal complexes and have followed Pauling's approach[37] to calculate corrections for differences in coordination number for a particular ion. Following Raymond's criteria, we have correlated the structural data for doubly and triply hydrogen-bridged metal-boron bonds with ionic radii for the metal ions obtained from Shannon's table.[38]

Table I and Table II list the available data for the compounds structurally characterized. The ionic radii as given in Tables I and II were obtained from Shannon's table for the particular oxidation state of the metal ion with the coordination number closest to that found in the metal borohydride complex. Corrections for coordination number were made as described by Raymond.[35] Plots of ionic radius vs. metal-boron distance are shown in Figures 1 and 2.

The lines in Figures 1 and 2 represent a linear least-squares fit to the data which were all assigned equal weight. For bidentate coordination the slope was equal to 0.97 with a correlation coefficient of 0.98. Note that both types of bidentate coordination (polymeric type and that with terminal H atoms) were included in Figure 1 and Table I. For tridentate coordination (Figure 2, not including the Th point), the slope was equal to 1.02 with a correlation coefficient of 0.94.

Considering the uncertainties in the metal ion-boron bond lengths, the different methods, temperatures, and phases for which structures were determined, the large range of coordination number and of the periodic table covered, plus the variety of other ligands attached to the metal atom, the correlation between ionic radius and the metal-boron bond length is remarkably good. For most molecules the metal-boron bond distance can be calculated with reasonable accuracy by using the ionic bonding model. Clearly, it is not possible to draw conclusions about covalent bonding between the metal atom and the borohydride group solely from structural considerations based on the metal-boron distance.

The one compound which does not fit this correlation is [((CH$_3$)$_3$Si)$_2$N]$_3$ThBH$_4$.[28] The Th ion is formally six-coordinate in this molecule, and the ionic radius obtained for the triple-hydrogen-bridged BH$_4^-$ group (unambiguously assigned

from the infrared spectrum)[28] is much too large (Figure 2). The bis(trimethylsilyl)amide group is an extremely bulky ligand which is known to form low coordination number complexes with metal ions of large ionic radii such as the lanthanides.[39] Although this ligand acts in a monodentate manner, it appears to have a much larger *effective* coordination number due to its steric bulk. From Figure 2 one can extrapolate an *effective* coordination number ≥12 for the Th ion in [((CH$_3$)$_3$Si)$_2$N]$_3$ThBH$_4$.

From the present tabulation it appears that an ionic radius of ~1.6 ± 0.1 Å can be assigned to the borohydride ligand when it forms a bidentate bridge to the metal atom and ~1.36 ± 0.06 Å when it forms a tridentate bridge to the metal atom. The difference in energy between the various possible modes of bonding is small, and the coordination number of the metal ion and the steric hindrance by other ligands appear to determine which mode of attachment will prevail for the borohydride ligand.

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Some Incorrect Space Groups: An Update

Sir:

Recently,[1] we noted that seven crystal structures reported in Volume 16 of *Inorganic Chemistry* (1977) had been described in space groups of unnecessarily low symmetry. We have now completed a similar survey of Volumes 17 and 18 (1978 and 1979), with the following results.

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