

plained in the following way. The failure of the lines due to the Fe(III),M(2) to narrow as  $H_{\text{app}}/T$  is increased suggests an additional source of broadening for these sites apart from relaxation broadening. This could be due to the presence of a range of hyperfine fields due to chemical disorder at the M(2) sites. As is discussed below and illustrated in Figure 13, each M(2) ion has four nearest neighbor M(2) sites which are occupied randomly by either Cd(II) or Fe(III). This random distribution could introduce local structural and magnetic disorder leading to a range of saturation fields. This disorder is consistent with the observed X-ray properties for voltaite.<sup>3</sup>

The different behavior of the internal hyperfine field on the two sites may be understood on the basis of the structure of  $\text{K}_2\text{Cd}_5\text{Fe}^{\text{III}}_3\text{Al}(\text{SO}_4)_{12}\cdot 18\text{H}_2\text{O}$ . The magnitude of the internal hyperfine field on a specific lattice site depends upon the contribution of the isotropic contact interaction arising from the polarization of the s-electron density by the 3d electrons, the contribution of the anisotropic noncontact interaction resulting from the 3d electron orbital moments, and the contribution of the anisotropic noncontact dipolar field of the 3d electron spin.<sup>32</sup> The latter two contributions are expected to be negligible for high-spin iron(III), and hence the first contribution must be primarily responsible for the differences in the magnitude of  $H_{\text{int}}$  for the two different iron(III) sites in this compound. The magnitude of this contribution is known to depend upon the covalency of the iron bonding, and covalency differences are believed to be responsible for the variation in  $H_{\text{int}}$  observed in a variety of high-spin iron(III) compounds.<sup>33</sup> In general, increasing covalency reduces  $H_{\text{int}}$  and increases the isomer shift (see above discussion). A comparison of the data for  $\text{K}_2\text{Cd}_5\text{Fe}^{\text{III}}_3\text{Al}(\text{SO}_4)_{12}\cdot 18\text{H}_2\text{O}$  presented in Tables III and IV indicates that at 4.2 K the Fe(III),M(2) site has a smaller  $H_{\text{int}}$  and a higher isomer shift than the M(1) site. This indicates that the covalency of the M(2) would be higher than that of the M(1) site. This conclusion is consistent with the

higher covalency expected for the  $\text{FeO}_4(\text{H}_2\text{O})_2$  coordination sphere of the M(2) site when compared with the  $\text{FeO}_6$  coordination sphere of the M(1) site. The postulated range of hyperfine fields at the M(2) sites could be due to differing covalency contributions.

The magnetic susceptibility results of Hermon et al.<sup>6</sup> indicate that  $\text{Ti}_2\text{CdFe}^{\text{III}}_3\text{Al}(\text{SO}_4)_{12}\cdot 18\text{H}_2\text{O}$  exhibits Curie-Weiss behavior down to ca. 3 K with a  $\theta$  value of -6 K. Their lowest temperature data reveal a small deviation of the inverse susceptibility toward the temperature axis in a manner similar to that found in voltaite.<sup>6</sup> This behavior is consistent with ferrimagnetic ordering (at a very low critical ordering temperature) of the spins on the two crystallographically different lattice sites. At these temperatures the antiparallel alignment of the spins on the M(1) and M(2) lattice sites would most likely result from a very weak antiparallel superexchange interaction via the sulfate groups that bridge the two lattice sites. As illustrated in Figure 13, a specific Fe(III),M(2) ion is linked to two nearest neighbor Fe(III),M(1) sites via four Fe-O-S-O-Fe pathways. Four similar pathways link the Fe(III),M(2) ion to four other nearest neighbor M(2) sites. It should be noted, however, that each of these nearest neighbor M(2) sites has only a 16.75% chance of containing an iron(III) ion, whereas both of the M(1) sites are occupied 100% by iron(III). As a result, we expect the interaction between M(2) and M(1) to predominate. The difference in magnitude of the internal hyperfine fields on the two sublattices would certainly be consistent with the ferrimagnetic interaction indicated in the magnetic susceptibility studies.<sup>6</sup>

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**Registry No.** Voltaite, 51747-83-2;  $\text{K}_2\text{Fe}^{\text{II}}_5\text{Fe}^{\text{III}}_3\text{Al}(\text{SO}_4)_{12}\cdot 18\text{H}_2\text{O}$ , 72638-81-4; cadmium voltaite, 72638-82-5;  $\text{K}_2\text{Cd}_5\text{Fe}_3^{\text{III}}\text{Al}(\text{SO}_4)_{12}\cdot 18\text{H}_2\text{O}$ , 72638-83-6.

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## Measurement of Boron Trihalide Electron Affinities: Correlation with Boron-Nitrogen Adduct Strengths

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The adiabatic electron affinities of several boron trihalides have been measured from the determination of threshold kinetic energies for the reaction  $\text{Cs} + \text{BX}_3 \rightarrow \text{Cs}^+ + \text{BX}_3^-$ . A crossed-molecular-beam apparatus was used. The electron affinities are <0.0, 0.33, 0.69, 0.94, and 0.82 eV for  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{BCl}_2\text{Br}$ ,  $\text{BClBr}_2$ , and  $\text{BBr}_3$ , respectively, with an error estimate of about  $\pm 0.2$  eV. These electron affinities are used to obtain B-N bond energies for adducts of boron trihalides with  $\text{Me}_3\text{N}$  by using an ionic energy cycle. Values are compared to direct measurements and to those estimated from NMR shift measurements.

### Introduction

Boron trihalide-amine adducts are classic examples of donor-acceptor bond behavior and illustrate an intriguing model of chemical bonding.<sup>1-4</sup> One step in the study of these adducts

is the determination of the relevant properties of the boron trihalides  $\text{BX}_2\text{Y}$ , where X may be the same as or different from

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Y. Our purpose is to report the measurement of electron affinities for several  $BX_2Y$ . Kinetic energy thresholds were obtained for the formation of parent negative ions as a result of collisions of beams of cesium and  $BX_2Y$ . This well-established procedure<sup>5</sup> yields adiabatic electron affinities.

The symmetric boron trihalides  $BX_3$  are planar species with  $XBX$  angles of  $120^\circ$ . They are very strong Lewis acids and react with Lewis bases to form adducts. The order of acid strength is  $BF_3 < BCl_3 < BBr_3 < BI_3$ . The textbook example of such adducts is  $Me_3N + BX_3 \rightarrow Me_3N \cdot BX_3$ , in which the  $XBX$  angles in the product become nearly tetrahedral.<sup>1-3</sup>

Mulliken<sup>4</sup> has described these adducts by using a wave function of the form  $\psi = a\psi_0(AB) + b\psi_1(A^-B^+)$ , where A and B are the acceptor and donor, respectively. For the case of  $X_3B \cdot NMe_3$ , the ionic form predominates: i.e.,  $b^2 > a^2$ . Mulliken states that "in general a strong donor B or acceptor A is one which tends to make  $b/a$  large. Since  $\psi$  refers to the ground state of AB,  $b/a$  tends to be larger the lower the energy of the structure  $\psi_1(A^-B^+)$  relative to  $\psi_0(AB)$ . The energy of  $A^- + B^+$  is obviously lower the smaller the ionization energy,  $I$ , of B and the larger the electron affinity,  $E$ , of A. Hence small  $I$  makes for a good donor and large  $E$  for a good acceptor. Additional factors are often important: in particular, the closeness to which the electrical center of gravity of oppositely charged ions can approach each other, or briefly, the mutual approachability. Thus a good donor should have small  $I$  and/or good approachability and a good acceptor, large  $E$  and/or good approachability."

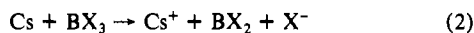
The major result of our study is that we find that the  $E(BX_3)$  are small, and "good approachability" appears to be the important factor in their strong Lewis acid behavior. This is understood in terms of the negative ion states involved as well as a simple model which provides a good correlation with several experiments.

### Experimental Section

Crossed molecular beams were used. An effusive beam of  $BX_2Y$  intersected a cesium beam whose kinetic energy was adjustable between 1 and 100 eV. The ionic products of the reaction were mass analyzed. The negative ion yield at a desired mass was recorded as a function of the Cs kinetic energy. These data led to kinetic energy thresholds in the center-of-mass system.

The experimental method, treatment of data, and energy calibration were those previously described<sup>6</sup> in a study of  $Cs + PX_3$ . Only a limited set of measurements were made with the  $BX_3$ , and the data are consequently less precise.

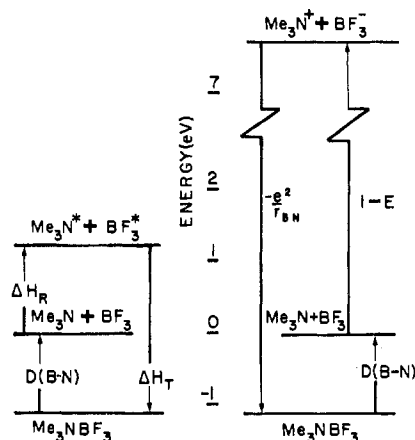
The crossed-beam reactions measured were



The value of  $I(Cs)$ , 3.893 eV, minus the measured threshold energies for reaction 1 equal the  $E(BX_3)$ , which are *adiabatic* electron affinities.<sup>5,7</sup>

### Results

Experiments with  $Cs + BF_3$  were previously described.<sup>7</sup> The only negative ion produced, at any energy, was  $F^-$ . The measured threshold energy was consistent with the mechanism of reaction 2. The failure to produce  $BF_3^-$  indicates that  $E(BF_3) \leq 0$ . An alternative explanation might be that transient  $BF_3^-$  ions are initially formed which have a positive



**Figure 1.** Alternative energy cycles for the formation of an  $Me_3N \cdot BF_3$  adduct from its ground-state constituents. At left, the  $Me_3N$  and  $BF_3$  are "reorganized" to have the same structures that they will have in the adduct and are then combined. At right, they are first converted to an ion pair, which then recombines.

electron affinity (i.e., that they are stable against electron detachment) but that they subsequently dissociate via reaction 2. However, the B-F bond energy is  $6.9 \pm 0.3$  eV<sup>8</sup> and  $E(F)$  is 3.4 eV,<sup>9</sup> so that if  $E(BF_3) \geq 0$ , the bond energy  $D(F_2B-F^-)$  would have to be  $>3.5 \pm 0.3$  eV. This high value is unlikely. For example, the  $D(Cl_2B-Cl^-)$  may be calculated from our  $E(BCl_3)$  (to be discussed later), from  $E(Cl) = 3.61$  eV,<sup>9</sup> and from  $D(Cl_2B-Cl) = 4.5 \pm 0.7$  eV<sup>8</sup> to be only  $1.2 \pm 0.7$  eV.

The dependence on the kinetic energy of the cross sections for reactions 1 and 2, with  $BCl_3$  and  $BBr_3$ , is similar to that with  $PCl_3$  which was shown in Figure 5 of ref 6. The cross section for  $BX_3^-$  formation rises rapidly with energy from threshold to a maximum and then decreases. The decrease is caused by the opening of competing reaction channel 2. At kinetic energies higher than about 10 eV above threshold the intensity ratio  $BX_3^-/X^-$  becomes quite small ( $<0.05$ ). This suggests that Franck-Condon transitions from  $BX_3$  reach a dissociative portion of the  $BX_3^-$  potential. At collision energies near threshold, however, some of the ions relax,<sup>5,7</sup> so that adiabatic electron affinities are derived.

The threshold energies are  $3.56 \pm 0.2$  and  $3.07 \pm 0.2$  eV for  $BCl_3^-$  and  $BBr_3^-$ , respectively, so that  $E(BCl_3) = 0.33 \pm 0.2$  eV and  $E(BBr_3) = 0.82 \pm 0.2$  eV. Threshold measurements were also made for  $BBrCl_2^-$  and  $BBr_2Cl^-$ . The  $BBrCl_2$  and  $BBr_2Cl$  molecules came from a mixture of  $BCl_3$  and  $BBr_3$ . The result is  $E(BBrCl_2) = 0.69 \pm 0.2$  eV and  $E(BBr_2Cl) = 0.94 \pm 0.2$  eV. These two species were investigated simultaneously, and because of cancellation of calibration errors, the difference  $E(BBr_2Cl) - E(BBrCl_2) = 0.25 \pm 0.1$  eV is more precise than are the absolute values.

Accordingly, the order of increasing electron affinities is  $BF_3 < BCl_3 < BBr_3$  and  $BBrCl_2 < BBr_2Cl$ . Calculations by Shriver and Swanson have previously suggested that  $E(BCl_3) > E(BF_3)$ ,<sup>10</sup> but calculation of the electron affinity is considered difficult.

### Discussion

Figure 1 displays two schematic energy cycles for adduct formation.<sup>11</sup> Both start with isolated  $BX_3$  and  $NMe_3$  in their normal geometry. At the left,  $\Delta H_R$  is required to "reorganize"

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**Table I.** Measured Electron Affinities  $E$  (eV),  $I - E$  Differences,<sup>a</sup> B-N Distances ( $r(\text{B-N})$ , Å), the NMR  $^1\text{H}$  Shift for  $\text{Me}_3\text{N}\cdot\text{BX}_3$  Adducts (Ppm), and the B-N Bond Energies  $D(\text{B-N})$  (kcal/mol)<sup>f</sup>

	$E$	$I - E$	$r(\text{B-N})$	$e^2/r(\text{B-N})$	$D(\text{B-N})$	NMR shift	$D^{\text{NMR}}(\text{B-N})$	$D(\text{B-N})$ lit.
$\text{BF}_3$	<0	>7.82 ± 0.2	1.636 <sup>c</sup>	8.80	>22.6	0.40 <sup>f</sup>	18.9	26.6, <sup>g</sup> 30.9 <sup>h</sup>
$\text{BCl}_3$	0.33 ± 0.2	7.49 ± 0.2	1.611 <sup>d</sup>	8.94	33.4 ± 5	0.78 <sup>f</sup>	36.9	30.5 (estd) <sup>g</sup>
$\text{BCl}_2\text{Br}$	0.69 ± 0.2	7.13 ± 0.2	1.61 <sup>e</sup>	8.94	41.8 ± 5	0.85 <sup>f</sup>	40.3	
$\text{BClBr}_2$	0.94 ± 0.2	6.89 ± 0.2	1.61 <sup>e</sup>	8.94	47.6 ± 5	0.89 <sup>f</sup>	42.2	
$\text{BBr}_3$	0.82 ± 0.2	7.00 ± 0.2	1.606 <sup>d</sup>	8.96	45.0 ± 5	0.95 <sup>f</sup>	(45.0)	
$\text{BI}_3$	(1.13) <sup>b</sup>		1.584 <sup>d</sup>	9.09		1.15 <sup>f</sup>	54.5	

<sup>a</sup> Reference 14.  $I$  is the ionization potential of  $\text{Me}_3\text{N}$ , 7.82 ± 0.02 eV. <sup>b</sup> Estimated from  $D^{\text{NMR}}(\text{B-N})$  and  $r(\text{B-N})$ , not measured here. <sup>c</sup> Reference 1. <sup>d</sup> Reference 2. See also M. Hargittai and I. Hargittai, *J. Mol. Struct.*, 39, 79 (1977). <sup>e</sup> Estimated from  $\text{BCl}_3$  and  $\text{BBr}_3$ . <sup>f</sup> B. Benton-Jones, M. E. Davidson, J. S. Hartmann, J. J. Klassen, and J. M. Miller, *J. Chem. Soc., Dalton Trans.*, 2603 (1972). <sup>g</sup> R. C. McCoy and S. H. Bauer, *J. Am. Chem. Soc.*, 78, 2061 (1956). <sup>h</sup> W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, 3, 164 (1956). <sup>i</sup>  $D(\text{B-N}) = e^2/r - (I - E)$ ,  $D^{\text{NMR}}(\text{B-N})$  from the shifts and normalized to our value for  $\text{BBr}_3$ , and  $D(\text{B-N})$  obtained from the literature.

isolated species to the geometries they will have in the adduct. This requires changing the  $\text{sp}^2$  hybridization in boron (planar) to  $\text{sp}^3$  (tetrahedral) with one vacant orbital. Additional energy is required if the  $\text{BX}_3$  is stabilized with  $\pi$  bonding, which is strongest in  $\text{BF}_3$ .<sup>12</sup> The final step  $\Delta H_7$  is the combination of these reorganized fragments to yield the homolytic bond energy  $D(\text{B-N})$ . This scheme has been the most popular in recent years.

An alternative cycle via charged particle intermediates<sup>4,11</sup> is shown at the right of Figure 1. The separated molecules are converted to an ion pair. This requires an energy  $I(\text{NMe}_3) - E(\text{BX}_3)$ . Here the adiabatic ionization potentials and electron affinities are used: i.e., the potential energies between the lowest neutral states and the lowest ionic states. (This contrasts with the related discussion of Mulliken<sup>4,13</sup> which requires vertical values.) The ion pair is then brought together to its measured internuclear distance. The largest energy term is the Coulombic  $-e^2/r$ , where  $r$  is the experimentally determined B-N distance. As will be discussed later, the reorganization energy of the negative ion is expected to be small. For the  $\text{Me}_3\text{N}\cdot\text{BX}_3$  systems the sum of these two terms leads to approximately the observed dissociation energies,  $D(\text{B-N})$ . Table I contains the measured B-N bond distances, the corresponding  $e^2/r$  term, and  $I(\text{Me}_3\text{N}) - E(\text{BX}_3)$ , where  $I(\text{Me}_3\text{N})$  is 7.42 ± 0.02 eV.<sup>14</sup> The effect of the increased electron affinities with mass is to lower the  $I - E$  level and to raise  $D(\text{B-N})$ .

Surprisingly, for this classic adduct system, few absolute values of  $D(\text{B-N})$  are found in the literature. These are listed in Table I. Lanthier and Miller<sup>15</sup> interpreted mass spectra and inferred that  $D(\text{B-N})$  increases with halogen as  $\text{I} > \text{Br} > \text{Cl} > \text{F}$ . More quantitatively, Miller and his associates<sup>16</sup> have reported that, for a particular base, there is a nearly linear relationship between  $D(\text{B-N})$  and the NMR shift for  $^1\text{H}$  as the X's are altered. The shifts reported<sup>16</sup> for the  $\text{BX}_2\text{Y}$  species studied here are shown in Table I. We have arbitrarily normalized this linear function to our calculated  $D(\text{B-N}) \equiv 45$  kcal/mol for  $\text{BBr}_3$  and computed a  $D^{\text{NMR}}(\text{B-N})$  for the other partners. Also shown are the previously measured values. The measured ratio for  $D(\text{B-N})$ 's with  $\text{BF}_3$  and  $\text{BCl}_3$  are inconsistent with the NMR shifts: however, the listed value for  $\text{BCl}_3$

is reported as "estimated". This procedure can be inverted to predict unknown electron affinities. As an example,  $E(\text{BI}_3)$  was estimated. While we observed  $\text{BI}_3^-$  in our experiments, the intensity was too low to measure  $E(\text{BI}_3)$ .

The advantages of the ionic energy cycle are (a) the physical existence of the separated ions so that their energies are measurable and (b) a leading term in the energetics of recombination that is simply  $-e^2/r$ . In contrast, the reorganized neutrals are hypothetical constructs whose energies must be calculated and whose recombination energy is not easy to obtain.

In order to use the ionic scheme, we require a system in which  $b$  is bigger than  $a$  [case 3 of Mulliken and Person (ref 4, p 225)], so that the ionic structure predominates.

The formation of free  $\text{BX}_3^-$  results in the deformation of the neutral  $\text{BX}_3$ . A calculation of Dewar and Rzepa<sup>17</sup> for  $\text{BF}_3$  indicates that the geometry of free  $\text{BF}_3^-$  is nearly that in the adduct. This means that most of the reorganization energy is included in the measured electron affinity. Brown et al.<sup>18</sup> calculate that the  $\pi$  bonding is only partially broken in the formation of reorganized  $\text{BX}_3$  and that  $\text{BF}_3$  requires 0.19 eV more than do  $\text{BCl}_3$  and  $\text{BBr}_3$ , which also suggests that the  $\text{BF}_3^-$  would be less stable than  $\text{BCl}_3^-$ .

The ionic scheme is crude: obvious refinements would be (a) correction for the small reorganization between the free ion and that in the adduct, (b) consideration of other electrostatic attraction terms and exchange forces, and (c) the effect of repulsive (steric) interactions. However, trends in a series may be discerned in which many of the errors cancel. Further, the individual steps in the cycle are convenient for the analysis. The electron affinities can be calculated independently or measured. The corrections required by the covalent contribution to  $\psi$  could be calculated.

However, it is difficult to escape the conclusion provided by this rather simple model. The constant component in the stability of many adducts is the charge separation and closeness of approach of the boron and nitrogen atoms while the electron affinity of the acceptor provides the basis for relative stabilities.

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**Registry No.**  $\text{BCl}_3$ , 10294-34-5;  $\text{BCl}_2\text{Br}$ , 13709-70-1;  $\text{BClBr}_2$ , 13709-71-2;  $\text{BBr}_3$ , 10294-33-4;  $\text{BI}_3$ , 13517-10-7;  $\text{Me}_3\text{N}\cdot\text{BF}_3$ , 420-20-2;  $\text{Me}_3\text{N}\cdot\text{BCl}_3$ , 1516-55-8;  $\text{Me}_3\text{N}\cdot\text{BCl}_2\text{Br}$ , 25889-90-1;  $\text{Me}_3\text{N}\cdot\text{BClBr}_2$ , 25889-91-2;  $\text{Me}_3\text{N}\cdot\text{BBr}_3$ , 1516-54-7;  $\text{Me}_3\text{N}\cdot\text{BI}_3$ , 5041-59-8;  $\text{BF}_3$ , 7637-07-2.

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