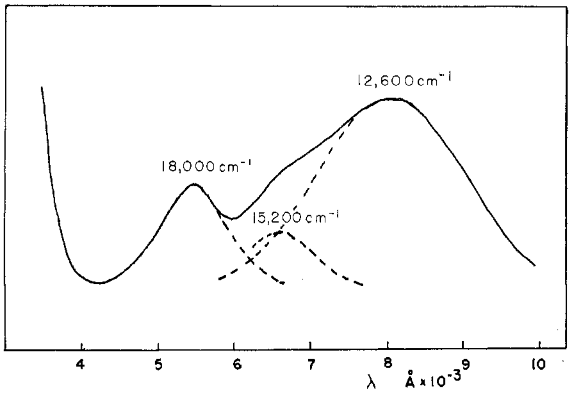

Figure 2.—Optical absorption spectrum of a freshly prepared solution of $VOSO_4$ in warm DMF.

$(CN)_5^{-3}$ would result in a ρ value smaller than the 1.39 value extrapolated from Figure 1 with $A = 79.9$ gauss. It is emphasized that the correlation may not lead to reliable values of ρ when the covalency is large, as for $VO(CN)_5^{-3}$, since ρ is calculated assuming an ionic model.

The correlation does not hold for low-symmetry vanadyl complexes. The interpretation of the e.s.r. spectra of low-symmetry vanadyl complexes is discussed elsewhere.[16]

Although the correlation (Figure 1) based on assigning the 18,000–26,000 cm.$^{-1}$ band as a $d_{xy} \rightarrow d_{z^2}$ transition is satisfactory, there is, of course, the possibility that this is actually a charge-transfer band with a behavior that parallels the $d_{xy} \rightarrow d_{z^2}$ transition. It seems unlikely that it could be the equatorial ligand-to-metal charge-transfer band since electron-withdrawing substituents such as CF_3 are found to lower the energy of this band (Table I) in the vanadyl acetylacetonates; it has, however, been shown[17] that electron-withdrawing substituents in the substituted acetylacetonates normally raise the energy of the ligand-to-metal charge-transfer band (note that vanadyl oxygen is not considered a ligand in our terminology).

It is more difficult to rule out the possibility that the transition is a charge transfer from the π orbitals of the vanadyl oxygen to the metal *xy* orbital. Both this charge-transfer transition and the z^2 transition are predicted to be $\perp$ polarized,[3] which appears to be the polarization found in the two cases that have been studied.[2,6] A recent extension of electron spin resonance theory to take into consideration charge-transfer states[18-22] suggests that this band is not the charge-transfer transition from the π orbital of vanadyl oxygen to the metal *xy* orbital since, if it were, there would be a positive contribution to the e.s.r. $g_\perp$ value such that the $g_\perp$ value would be expected to be near 2.0023.[18]

TABLE II

σ AND π ELECTROSTATIC INTERACTIONS FOR VYX_5 COMPOUNDS

Compound	σ_x, cm.$^{-1}$	π_x, cm.$^{-1}$	σ_y, cm.$^{-1}$	π_y, cm.$^{-1}$
$VO(NCS)_5^{-3}$	29,480[b]	12,280[b]	43,580[b]	66,280[b]
VOF_5^{-3}	22,920[b]	8,280[b]	35,220[b]	62,020[b]
$VOSO_4$	23,540[a]	7,540[a]	107,540[a]	59,560[a]

[a] Using optical assignment of ref. 2. [b] Using optical assignment proposed in this paper.

The experimental $g_\perp$ values are 1.9813 for $VOSO_4$,[14] 1.9745 ± 0.005 for $VO(CF_3CF_3acac)_2$ in DMF,[15] 1.9847 for $VOCl_5^{-3}$,[12] 1.979 for $VO(acac)_2$,[14] 1.977 ± 0.005 for $VO(NCS)_5^{-3}$ in DMF,[15] and 1.9846 ± 0.005 for $VO(CN)_5^{-3}$ in KBr.[15] These values cannot be explained by using a charge-transfer scheme putting the vanadyl oxygen-to-metal charge-transfer transition at high energy for $VOSO_4$ and at low energy for $VO(CF_3CF_3acac)_2$ unless one assumes that the V=O bond is highly ionic, which would be unexpected.

In addition to the ratio of the axial to equatorial field strength it is also possible to determine the field strength of the various ligands for MX_5Y systems using the expressions of Yamatera.[23] Defining σ_x as the σ electrostatic effect due to the σ bond between ligand X and M and π_x as the electrostatic effect due to the π bond between ligand X and M, he obtains the following expressions for the d orbital energy levels: $E_{xz} = E_{yz} = {}^3/_4\pi_x + {}^1/_4\pi_y$, $E_{xy} = \pi_x$, $E_{x^2-y^2} = \sigma_x$, and $E_{z^2} = {}^2/_3\sigma_x + {}^1/_3\sigma_y$ for MX_5Y type ions. It is not possible to solve directly for σ_x, π_x, σ_y, and π_y since there are four unknowns and three experimental absorption bands. To reduce the number of unknowns we have made the assumption in our calculations that the ratio of σ_x to π_x in VOX_5 is the same as for the corresponding ligand in Co(III).[24] Our data are given in Table II. The π_y values indicate considerable V=O π bonding while the σ_y values indicate a more normal V=O σ bond (the corresponding values for O^{-2} in CoO^+ are[22] $\sigma_y = 39{,}000$ cm.$^{-1}$ and $\pi_y = 24{,}000$ cm.$^{-1}$).

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Interaction of Decaborane and Aqueous Ammonia

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Decaborane reacts rapidly with aqueous hydroxide ion to form the $B_{10}H_{13}^-$ ion. Salts of this ion have been isolated from solution and have been well characterized and shown to be free of solvent.[1] However, if the solution ages[2] and then a salt is precipitated, the salt tends to be solvated as judged by analysis and infrared spectral data. Thus, there is the possibility that there is an intermediate between $B_{10}H_{13}^-$ and its hydrolysis product $B_9H_{14}^-$ which is a solvated $B_{10}H_{13}^-$ species.[3] We have evidence for such a solvate from a characterization of the aqueous decaborane–ammonia system.

In the dissolution of decaborane in aqueous ammonium hydroxide, two moles of base per mole of decaborane is required. The product is a monovalent anion that yields a cesium salt analyzing for $CsB_{10}H_{13}NH_3$. The chemistry of this species rather firmly establishes that it is not a member of the $B_{10}H_{14}^{2-}$ structural class. The ammonia is not firmly bound in this ion. Hydrolysis in water is quite rapid, and the hydrolysis product is $B_9H_{14}^-$. Cyanide ion immediately converts the labile $B_{10}H_{13}NH_3^-$ to the $B_{10}H_{13}CN^{2-}$ ion.[4]

It is unlikely that the ammonia molecule in labile $CsB_{10}H_{13}NH_3$ simply occupies a lattice site or is coordinated to the cesium cation. This ion shows ultraviolet absorption maxima at essentially the same wave lengths as does $B_{10}H_{13}^-$. However, the extinction coefficient of the 335 mμ absorption is about one-third that reported for $B_{10}H_{13}^-$. Thus, the introduction of ammonia into this system has perturbed the electronic structure of $B_{10}H_{13}^-$. The infrared and B^{11} n.m.r. spectra of $CsB_{10}H_{13}NH_3$ are significantly different from those of $B_{10}H_{13}^-$. Furthermore, the interaction of hydroxide ion with $B_{10}H_{13}NH_3^-$ suggests that the ammonia may be bound in some fashion to the $B_{10}H_{13}^-$ ion. Interaction of hydroxide ion with $B_{10}H_{13}NH_3^-$ does not yield the $B_{10}H_{13}OH^{2-}$ ion[5] but yields a new ion of the same composition as the starting material, that is, $B_{10}H_{13}NH_3^-$. This new ion is believed to be a member of the $B_{10}H_{14}^{2-}$ structural class. It is quite resistant to hydrolysis as is typical of this particular structural class. The ammonia molecule is not susceptible to displacement by other nucleophiles such as cyanide ion, and finally acid degradation of this ion does not yield $B_9H_{14}^-$,[5,6] but rather $B_9H_{13}NH_3$. The B^{11} n.m.r. spectrum is similar to that of other members of this structural class.

Experimental Section

Labile $CsB_{10}H_{13}NH_3$.—Decaborane (15.8 g. 0.13 mole) was added in small portions to 250 ml. of concentrated ammonium hydroxide solution, a small amount of insoluble residue was removed by filtration, and a solution of 25 g. of cesium fluoride in 50 ml. of water was added to the filtrate. The white precipitate was collected by filtration, washed with methanol and ether, and air dried. The yield of $CsB_{10}H_{13}NH_3$ was 31 g. (89%). *Anal.* Calcd. for $CsB_{10}H_{13}NH_3$: Cs, 49.0; B, 39.9; H, 6.0; N, 5.2. Found: Cs, 46.7, 47.4; B, 38.7, 38.6; H, 6.1, 6.3; N, 5.3, 4.9. Platinum-catalyzed acidic hydrolysis gave 1758 ml. of H_2/g. of compound compared with a calculated amount of 1817 ml./g.

The lifetime of $CsB_{10}H_{13}NH_3$ in water is only a few minutes but is significantly longer in a mixture of 80% acetonitrile and 20% water. In this medium, $CsB_{10}H_{13}NH_3$ absorbs radiation at 262 mμ (ε 2870) and 335 mμ (ε 634). The infrared spectrum of $CsB_{10}H_{13}NH_3$ shows N–H stretching at 3290, 3250, and 3165 cm.$^{-1}$, B–H stretching at 2470 cm.$^{-1}$ with a shoulder at 2355 cm.$^{-1}$, N–H deformation at 1575 cm.$^{-1}$ with a shoulder at 1600 cm.$^{-1}$; other absorptions were observed at 1395 (vs), 1193 (s), 1089 (m), 1078 (sh), 1037 (s), 1010 (sh), 950 (m), 910 (m), 885 (w), 855 (w), 817 (w), 795 (w), 760 (w), 741 (w), and 695 (w) cm.$^{-1}$.

The B^{11} n.m.r. spectrum (19.25 Mc.—trimethyl borate external reference) consists of a low-field doublet of intensity 1 at 11.9 p.p.m. which overlaps a doublet of intensity 7 (J_{BH} = 129 c.p.s.) at 23.8 p.p.m. and a high-field doublet of intensity 2 at 53.7 p.p.m. (J_{BH} = 137 c.p.s.).

Stable $CsB_{10}H_{13}NH_3$.—Recrystallization of labile $CsB_{10}H_{13}NH_3$ from a 50% potassium hydroxide solution gave a colorless, crystalline solid of the same composition. *Anal.* Found: Cs, 47.7, 48.3; B, 39.8, 40.1; H, 6.0, 6.1; N, 5.1, 5.1; hydrolytic hydrogen, 1848 ml./g. Recrystallization of $CsB_{10}H_{13}$ or $CsB_{10}H_{13}(CH_3OCH_2CH_2OCH_3)_x$ from cesium hydroxide solution gave $Cs_2B_{10}H_{13}OH$. *Anal.* Calcd. for $Cs_2B_{10}H_{13}OH$: Cs, 65.8; B, 26.8; H, 3.48; O, 3.96. Found: Cs, 65.4; B, 26.4; H, 3.68; O, 4.13 ($KBrF_4$).

Mr. K. Babcock indexed stable $CsB_{10}H_{13}NH_3$ as orthorhombic (Z = 4) with the space group $P2_12_12$ and cell indices of a = 12.184, b = 11.525, and c = 7.580 Å. With an experimental density of 1.70, the calculated molecular weight is 272.5 compared to the theoretical value of 271.3. The X-ray powder pattern of stable $CsB_{10}H_{13}NH_3$ is distinctly different from that of the labile species. The ultraviolet absorptions in water are at 223 mμ (ε 7000) and 250 mμ (ε 5660). In the infrared spectrum of stable $CsB_{10}H_{13}NH_3$, the N–H stretching absorption is a doublet at 3290 and 3205 cm.$^{-1}$, the B–H stretching absorption at 2500, 2465, 2410, and 2340 cm.$^{-1}$, and the N–H bending at 1592 cm.$^{-1}$ Other bands were observed at 1408 (s), 1182 (m), 1130 (w), 1081 (m), 1025 (s), 966 (w), 930 (w), 910 (w), 875 (w), 806 (w), 720 (m), and 650 (w) cm.$^{-1}$.

The B^{11} n.m.r. spectrum in water has a broad, low-field peak at 26.1 p.p.m. which partially overlaps another multiplet centered at 39.7 p.p.m.; the total relative intensity is 8. There is a well-resolved, high-field doublet of intensity 2 at 60.2 p.p.m. (J_{BH} = 134 c.p.s.).

$B_9H_{13}NH_3$.—Recrystallized $CsB_{10}H_{13}NH_3$ (4.0 g., 0.016 mole) was dissolved in 200 ml. of warm water, and 10 ml. of 30% hydrochloric acid was added over a period of 1 hr. Hydrogen was evolved during the acid addition, and $B_9H_{13}NH_3$ precipitated. The solid (~1 g.) was collected by filtration and was recrystallized from hot water and from benzene, m.p. 162–163° dec. *Anal.* Calcd. for $B_9H_{13}NH_3$: B, 76.4; H, 12.7; N, 11.0; mol. wt., 127.5. Found: B, 75.7; H, 12.2; N, 10.6; mol. wt., 116, 119 (cryoscopic in $(CH_3)_2SO$). Ebullioscopic determinations in benzene and acetone consistently gave high values, ~170–180, for the molecular weight.

The ultraviolet absorption in water is at 267 mμ (ε 3940). The infrared spectrum consists of the following bands (cm.$^{-1}$): 3290, 3265, and 3210 (N–H stretching), 2520 (B–H stretching), 1590 (N–H deformation), 1440 (broad, m), 1400 (sharp, s), 1364 (broad, m), 1150 (m), 1106 (w), 1047 (sh), 1025 (m), 1005 (m), 909 (broad, m), 838 (w), 785 (w), 755 (w), 700 (broad, w) cm.$^{-1}$. The B^{11} n.m.r. spectrum consists of two overlapping, low-field doublets at 7.8 and 17.6 p.p.m. which upon irradiation at 60 Mc. collapse into two single peaks each of intensity 1, a multiplet centered at 36.5 p.p.m. of intensity 5, and a high-field doublet of intensity 2 at 57.4 p.p.m. (J_{BH} = 149 c.p.s.).

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[2] The aging period must be less than the time in which $B_9H_{14}^-$ formation becomes significant.

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