Table I

Infrared Absorption Bands of Reported Borazines (cm.$^{-1}$)

$(CH_3BNH)_3$	$(CH_3)_4B_6N_6H_4$	Condensed borazine A	Condensed borazine B
3440	3450	3450	3470
2960	2960	2960	2960
1605			
1490	1470	1490	1470
	1410	1446	
1336		1342	1334
1300	1316	1310	
	1200	1230	
	1185		
	1160		1162
	1122	1120	1103
1082	1080	1087	
893	893	893	893
	827	827	
784	806	775	
720	720	715	
		685	698

the yield of B-trimethylborazine by running the Grignard reaction in diethyl ether at low temperature were not successful. Below −45° the formation of solids prevents stirring. If mixed at −45° and warmed slowly to about −38°, an exothermic reaction occurs which rapidly heats the mixture to the reflux temperature. Several such experiments, starting with one mole of B-trichloroborazine in each case, gave 17.90 g. and 20.35 g. of B-trimethylborazine and 8.00 g. and 4.80 g. of I.

Reaction of Highly Purified B-Trichloroborazine with Methylmagnesium Bromide.—In order to be sure that the borazine condensation was occurring during the Grignard reaction and not prior to it the B-trichloroborazine was very carefully purified by recrystallization from carbon tetrachloride. The chloride analysis (57.4%; calcd. 57.85%) and the melting point (83.9–84.6°; lit.[10] m.p. 83.9–84.5°) were indicative of high purity. The yields of B-trimethylborazine (30.30 g.) and the bicyclic borazine I (15.46 g.) were essentially the same as those resulting from other preparations.

Infrared Spectra.—The infrared absorption bands of these four borazines were obtained using a Perkin-Elmer Infracord and are recorded in Table I. The first two rows obviously arise from the N–H and C–H absorptions. However, the placement of bands in the other rows is merely intended to indicate similarity and not necessarily the correlation of any specific energy transitions.

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Assignment of Optical Spectra for Vanadyl Complexes[1]

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Recently there have been a number of experimental and theoretical discussions of the energy levels and optical spectra of vanadyl complexes from which several alternate assignments of the optical spectra have been made.[2–6] In this note we wish to present an empirical correlation between e.s.r. hyperfine splittings and values of the ratio of axial to equatorial charge obtained from optical spectra which makes possible a consistent set of optical assignments. This was suggested by our previous work on the e.s.r. spectra of substituted copper(II) acetylacetonates[7] in which it was found that two dissimilar copper(II) complexes which had similar e.s.r. A values also had similar optical absorption spectra.

From crystal field theory and an ionic model it is possible to determine the ratio ρ of the axial charge to the equatorial charge[8] defined as

$$\rho = \frac{\rho_4^{+z} + \rho_4^{-z}}{2\rho_4^{xy}} \qquad (1)$$

where ρ_4^{+z} is the field strength along the V=O axis, ρ_4^{-z} is the field strength *trans* to the V=O position, and ρ_4^{xy} is the in-plane field strength[9]; ρ is obtained from the experimental optical spectra by use of the equation[8]

$$\rho = \frac{3(E_{xy\rightarrow z^2}) - 4(E_{xy\rightarrow xz,yz})}{2(E_{xy\rightarrow x^2-y^2})} - {}^1/_2 \qquad (2)$$

The optical band for vanadyl compounds which normally lies between 18,000 and 26,000 cm.$^{-1}$ has been variously assigned as the $d_{xy} \rightarrow d_{z^2}$ transition[8] or as a charge-transfer band.[3,6] If it is uniformly assigned as the d–d transition, and if the values of ρ computed on this basis are plotted against the e.s.r. hyperfine splittings A for the vanadium nucleus for a series of vanadyl compounds (Figure 1), the points fall close to a straight line. Since this series (Table I) covers a wide range of vanadyl–ligand bond types, from the more ionic $[VOF_5]^{-3}$ to the more covalent $[VO(NCS)_5]^{-3}$, the excellent correlation appears to be significant. If this is so one may then use the observed e.s.r. A values to obtain ρ from Figure 1 as a check on future vanadyl optical assignments or to determine the position of the $d_{xy} \rightarrow d_{z^2}$ transition if it is buried under the shoulder of an intense charge-transfer band. The data and assignments chosen in drawing Figure 1 are summarized in Table I and two extensions, to the largest known e.s.r. A value, $VOSO_4$, and the smallest, $VO(CN)_5^{-3}$, are discussed below.

However, before discussing the two extensions we wish to point out that the relative changes in ρ are those expected from a consideration of other data and the physical model of the complexes. The increase in ρ value in going from vanadyl sulfate to vanadyl acetylacetonate is consistent with the decrease in the

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Table I

Energy Levels, E.s.r. Hyperfine Splittings, and ρ Values for Vanadyl Complexes

Compound	No. in Fig. 1	$E_{xy\to xz,yz}$, cm.$^{-1}$	$E_{xy\to x^2-y^2}$, cm.$^{-1}$	$E_{xy\to z^2}$, cm.$^{-1}$	ρ	A, gauss
$VO(CN)_5^{-3}$ in H_2O					1.39	79.9[a]
$VO(acac)_2$ in CH_3OH[i]	1	13,000[b]	17,450[b]	25,600[b]	0.210	102.3[c]
$VO(acac)_2$ in DMF	2	13,000[b]	17,000[b]	25,100[b]	0.185	104.4[a]
$VO(NCS)_5^{-3}$	3	13,500[d]	17,200[d]	23,900[d]	0.145	104.75[a]
$VO(acac)_2$ in CH_3CN	4	14,200[b]	16,800[b]	25,800[b]	0.113	105.3[c]
$VO(acac)_2$ in CH_3COCH_3	5	14,300[c]	16,700[c]	25,600[c]	0.888	106.0[c]
$VO(acac)_2$ in $CHCl_3$	6	14,900[b]	16,900[b]	26,000[b]	0.041	106.4[c]
$VO(oxalate)_2$ in DMSO	7	12,400[a]	16,000[a]	22,900[a]	0.046	106.9[a]
$VOCl_5^{-3}$	8	15,500[e]	16,200[e]	26,000[e]	−0.006	109.4[f]
$VO(acac)_2$ in C_6H_6	9	15,300[b]	16,900[b]	25,700[b]	−0.030	108.3[a]
$VO(CF_3acac)_2$ in C_6H_6	10	14,700[a]	16,800[a]	23,500[a]	−0.102	110.4[a]
$VO(CF_3CF_3acac)_2$ in $CHCl_3$	11	13,400[a]	16,200[a]	20,700[a]	−0.240	112.6[a]
$VOSO_4$ in DMF	12	12,600[a]	15,200[a]	18,000[a]	−0.382	114.6[a]
VOF_5^{-3} in HF, H_2O	13	13,300[g]	14,100[g]	18,200[g]	−0.450	116.0[a]
$VOSO_4$ in dil. H_2SO_4		13,230[h]	(11,700)[h]	16,200[h]	−0.440	116[h]

[a] H. A. Kuska and M. T. Rogers, unpublished results. [b] Ref. 8. [c] I. Bernal and P. H. Rieger, *Inorg. Chem.*, **2**, 256 (1963). [d] In CH_3CN: L. H. Holmes, Jr., Thesis, Louisiana State University, 1961. [e] In $K_3TlCl_6 \cdot 2H_2O$: ref. 6. [f] In $(NH_4)_2[In\,Cl_5 \cdot H_3O]$: ref. 12. [g] In KBr pellet: ref. 3. [h] Ref. 11. [i] The symbol acac is used for acetylacetone, CF_3acac for trifluoroacetylacetone, CF_3CF_3acac for hexafluoroacetylacetone, DMF for dimethylformamide, and DMSO for dimethyl sulfoxide.

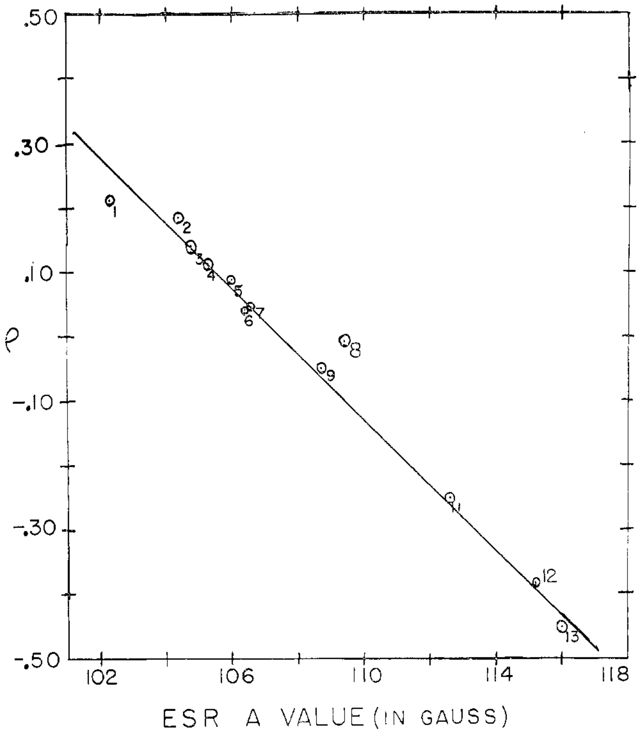

Figure 1.—Plot of vanadium hyperfine splittings (A) for a series of vanadyl complexes *vs.* the ratio ρ of axial to equatorial charge computed from optical data using crystal field theory. The optical assignments used in computing ρ are those of Table I.

vanadium–oxygen double bond distances, 1.67[10a] and 1.59 Å.[10b], respectively, obtained from X-ray spectroscopy. Also, the increase in ρ obtained as vanadyl acetylacetonate is dissolved in more polar solvents is what one might expect from the consideration that there is an empty axial position which can become occupied by coordinating solvents.

For $VOSO_4$, using the reported e.s.r. A value[11] and the corresponding ρ value extrapolated from Figure 1, it appears that the 16,200 cm.$^{-1}$ [10] band is the $xy \rightarrow z^2$ transition. This assignment is supported by the polarization of this band.[2] In C_{4v} symmetry the $xy \rightarrow z^2$ transition is expected to be allowed with $\perp$ polarization while the $xy \rightarrow x^2 - y^2$ transition is allowed both $\|$ and $\perp$.[12] It therefore appears that the 13,230 cm.$^{-1}$ band contains two components, the $xy \rightarrow xz, yz$ and the $xy \rightarrow x^2 - y^2$ transitions as had been suggested previously.[3] This assignment is consistent with the reported solvent effect on the positions and intensities of the $VOSO_4$ optical bands.[11,13]

As one goes from H_2O to 100% H_2SO_4 the higher energy band goes from 16,000 cm.$^{-1}$ and an extinction coefficient (ϵ) of 8 to $\simeq$14,500 cm.$^{-1}$ (ϵ 18), while the lower energy band goes from $\simeq$13,000 cm.$^{-1}$ (ϵ 18) to $\simeq$12,700 cm.$^{-1}$, (ϵ 12). Although this behavior has been interpreted as a crossing of the bands,[13] it is also possible that one of the $\simeq$13,000 cm.$^{-1}$ transitions (probably the $xy \rightarrow x^2 - y^2$) is shifted to $\simeq$14,500 cm.$^{-1}$.

The optical spectrum of $VOSO_4$ in DMF is given in Figure 2. It is now possible to resolve the three expected peaks so the correlation apparently continues to hold for this case, providing evidence that the energy levels for $VOSO_4$ in H_2O are as predicted by the correlation (Table I) rather than as predicted by the theoretical Wolfsberg–Helmholz type calculation.[2]

The correlation of Figure 1 is in agreement with the suggestion by Kivelson and Lee[14] that the principal dependence of the e.s.r. A value is on the energy level separations rather than on the covalency as is normally expected. However, for $VO(CN)_5^{-3}$ the covalency contribution may be significant since a ^{13}C e.s.r. hyperfine splitting of 11.3 gauss is observed.[15] Correcting the vanadyl e.s.r. A value for covalency effects in VO-

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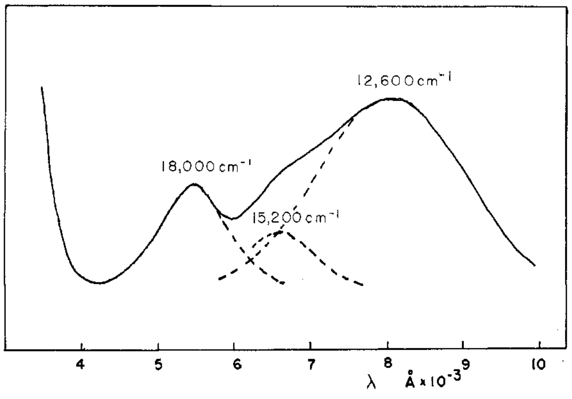

Figure 2.—Optical absorption spectrum of a freshly prepared solution of $VOSO_4$ in warm DMF.

$(CN)_5^{-3}$ 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.$^{-1}$).

Acknowledgment.—We are indebted to Mr. R. L. Wegener, who obtained the optical spectrum of vanadyl oxalate, and Mr. R. E. Drullinger, for the optical spectrum of $VOSO_4$ in DMF.

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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