probably due to the equilibrium condition described by the reaction

$$2B(OH)_3 + B(OH)_4 \rightleftharpoons B_3O_3(OH)_4^- + 3H_2O \qquad (6)$$

and represents the polyanion $B_3O_3(OH)_4^-$. The high-field peak then represents the polyanion $B_5O_6(OH)_4^-$.

A solution of potassium pentaborate shows two absorptions at concentrations up to saturation at room temperature. These absorptions correspond to the two low-field absorptions in the sodium pentaborate spectra. If a saturated potassium pentaborate solution is prepared at 30°, a third absorption is observed which corresponds to the high-field absorption in the sodium pentaborate spectrum (Figure 4). Unfortunately, our nmr spectra are not sufficiently resolved to permit quantitative calculations of equilibrium constants, although this should be possible with the aid of Fourier transform techniques. An estimate of the areas under the peaks in the pentaborate spectra (Figure 3) allowed a calculation of the ratio of boron atoms in the high-field peak to those in the low-field peaks, an exercise carried out by Momii and Nachtrieb. Our results were in rather poor agreement with those reported previously.[1] We also found it difficult to obtain an accurate value for the chemical shift at infinite dilution for tetraborate solutions although a reasonable estimate did appear to be $\delta_{Na_2B_4O_7}$ 9.0 ± 0.5, in agreement with the value reported by Momii and Nachtrieb. Assuming the equilibria proposed by Momii and Nachtrieb (eq 1–3) and using the value 10^5 for K_1, we obtained values of pK_3 and pK_5 which were approximately 20 and 50% lower, respectively.

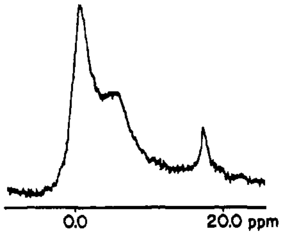

Figure 4.—The ^{11}B nmr spectrum of a saturated $K_2O \cdot 5B_2O_3 \cdot 8H_2O$ solution at 30.0°.

It is interesting to note that the chemical shifts of the high-field absorptions in both the tetraborates and pentaborates have approximately the same values. If one estimates the position of the low-field absorption in tetraborates and compares it with the position of the middle absorptions of the pentaborate spectra, a similar correlation is seen. This suggests that two stable polyborate species occur in both tetraborate and pentaborate solutions and that they are identical. The high-field absorption +18 ppm probably represents $B_5O_6(OH)_4^-$ as suggested by Momii and Nachtrieb while the absorption at approximately 6 ppm could represent the $B_3O_3(OH)_4^-$ species not observed by Momii and Nachtrieb but postulated as one of the species involved in a rapid interchange of boron among three distinct sites. It is hoped that with the aid of Fourier transform spectroscopy we will be able to obtain quantitative equilibrium data in the near future.

Experimental Section

Chemicals.—All of the borates used in this work were special quality products produced by U. S. Borax and Chemical Corp.

Spectrometer.—The 80-MHz ^{11}B nmr spectra were obtained on an instrument designed by Professor F. A. L. Anet, Department of Chemistry, University of California, Los Angeles, Calif.

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Preparation and Characterization of Phosphitochromium(III)

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In a recent study of the reduction of Cr(VI) in excess hypophosphorous acid,[1] we observed that the Cr(III) product was formed as cationic complexes both of P(I) and P(III). Characterization of the 1:1 complex between Cr(III) and hypophosphite has been reported by Espenson and Binau;[2] and although complexes between Cr(III) and phosphite have been reported by Ebert and Podlaha,[3] their work dealt with the solid state and solutions of pH 6 or greater. A more detailed study of the 1:1 complex formed between Cr(III) and P(III) in acidic media was undertaken as a basis for further study of the products of Cr(VI) reductions.

Experimental Section

Reagents and Preparation.—Commercially available chromium(III) perchlorate was recrystallized from dilute $HClO_4$; sodium perchlorate was recrystallized from water. Calcium perchlorate was prepared from calcium carbonate and $HClO_4$ and was recrystallized. Water was redistilled from alkaline permanganate and other reagents were used without further purification. Chromium and phosphite analyses were performed as previously described.[1]

Solutions of monophosphitochromium ion, presumably, phosphitopentaaquochromium(III), $Cr(H_2O)_5(O_3PH_2)^{2+}$, were prepared as follows. A solution *ca.* 0.4 *F* in both chromium perchlorate and phosphorous acid was deoxygenated in a stream of N_2 and was then heated in a stoppered flask to 45° for 6–8 days. The desired complex was separated from the cooled reaction mixture containing Cr^{3+} and P(III)–Cr(III) complexes by cation exchange. Espenson, *et al.*,[2] reported a very low flow rate was required for good separation of their P(I)–Cr(III) complex from by-products. We used, successively, two columns, each with about 50% excess resin capacity, for the separation and flow rates of up to 0.3 ml/min. In the primary separation, species of charge 1+ or less were eluted with 0.3 *F* $HClO_4$, after which 0.5 *F* $Ca(ClO_4)_2$ was used to displace the 2+ and 3+ species. The central 90% of the dark green band preceding the purple Cr^{3+} was collected, placed on a smaller secondary column, and eluted with 0.8 *F* $HClO_4$. Initially, high P(III):Cr(III) ratios and anomalous spectral results led us to suspect small quantities of another, presumably polymeric, P(III)–Cr(III) complex were contaminating the leading edge of the 2+ band; portions of the effluent of the secondary preparation column were diluted and their absorbances were measured with a Beckman DU at 418 and 420 nm. Samples for which $A_{420} \neq A_{418}$ were rejected. In general the central 90% of the 2+ band on the second column was collected. The product was typically 0.15

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F in Cr(III) and 0.5 *M* in hydrogen ion. The total yield based on initial Cr(III) was 10–15%. The P(III):Cr(III) ratio of the product was 0.99 ± 0.01. The elution characteristics of the complex on a column in the H^+ form were clearly consistent with a 2+ ionic charge. However, attempts to measure the charge per Cr ratio in dilute solutions gave values between 2+ and 1+ suggesting partial deprotonation of the complex (*vide infra*).

In the visible and ultraviolet spectral regions, phosphitochromium(III) in 0.7 *F* $HClO_4$ has absorption maxima (nm) and molar absorptivities (M^{-1} cm^{-1}) very close to those of hypophosphitochromium(III):[2] 596 (15.4), 419 (16.8), and 267 (5.5). At wavelengths shorter than 250 nm, the molar absorptivity of the complex rises sharply and is sensitive to the presence of traces of the 2+ contaminant largely eliminated in the second-column separation.

Equilibrium Studies.—A charge per Cr ratio less than 2, pH 1.5–3, suggested a rapid equilibrium was established among the complex, hydrogen ion, and a deprotonated species, presumably, $Cr(O_3PH)^+$, according to equilibrium 1. To prepare a solution

$$Cr(O_3PH_2)^{2+} \rightleftarrows Cr(O_3PH)^+ + H^+ \tag{1}$$

containing predominantly the deprotonated species, a solution of the complex prepared as described above was stirred magnetically while anion resin in the acetate form was slowly added. The pH was continuously monitored and addition was halted at pH 3.5. The resin was quickly filtered off and the filtrate was placed on a cation column in the Na^+ form. The complex was rinsed with distilled water and then easily eluted with $NaClO_4$, 0.25 *F*, consistent with a 1+ ionic species. The pH of the column effluent containing the product was 3.5–3.0, and properties on addition of excess $HClO_4$ were the same as for the original preparation.

The spectrum of the complex in 0.7 *F* $NaClO_4$ was recorded over a wide range of hydrogen ion concentrations, adjusted with dilute perchloric acid. Solution pH was measured with a research grade pH meter, calibrated against solutions of known $[H^+]$ and the same ionic strength. In the visible spectral region, the complex at pH 3.3 had maxima and apparent molar absorptivities of 589 (18.1) and 422 (17.9). In the ultraviolet region, the absorptivity rose steeply at wavelengths less than 270 nm, with a shallow shoulder at 268 nm. The apparent molar absorptivities at pH 3.3 were uniformly greater than those at pH 0.3 so that no isosbestic point was observable. A referee has pointed out that the constant ratio of absorptivity changes with increasing $[H^+]$ at the three wavelengths supports[4] our assumption of only two absorbing species.

The acid dissociation quotient for equilibrium 1 was estimated from the absorbance of these solutions at 590, 422, and 270 nm. The data presented in Table I are consistent with $Q_a(Cr(O_3PH_2)^{2+}) = (2.3 \pm 0.2) \times 10^{-3}$ *M*.

TABLE I

APPARENT MOLAR ABSORPTIVITIES OF SOLUTIONS OF $Cr(O_3PH_2)^{2+}$ AT 25° AND IONIC STRENGTH 0.7 *F*

	$10^3[H^+]$, *M*				
	0.507	5.20	11.0	30.5	630
ϵ_{590}	18.10	16.49	16.01	15.61	15.38
ϵ_{422}	17.92	17.07	16.88	16.68	16.56
ϵ_{270}	7.36	6.06	5.76	5.38	5.23

Aquation.—Samples of the complex in 0.3–1.0 *F* $HClO_4$ were deoxygenated with a stream of N_2 and heated to 45°. Aquation was observed by placing an aliquot of the sample on a small cation column and determining the P(III) content of the combined rinsings. The residue on the column was rinsed with 0.9 *F* $HClO_4$ and examined for evidence of aquation products. In addition to the expected Cr^{3+} and unaquated $Cr(O_3PH_2)^{2+}$, a small green band above the Cr^{3+}, evidently with a charge 3+ or greater, was observed in samples taken from freshly synthesized complex. Samples for which 24 hr or more elapsed between the primary and secondary synthetic separations showed at most only a faint trace of this green band; we believe it to be an artifact of the synthesis and tentatively interpret it as a rapidly formed hydrolysis product of a dipositive polychromium(III) complex. Apparent pseudo-first-order rate constants, 10^7k (sec^{-1}), for aquation of $Cr(O_3PH_2)^{2+}$ at 45° and $[H^+]$ = 0.3 and 1.0 *M* are respectively 0.4 and 1.4. Kinetics were not further pursued.

Discussion

The similarity in the visible and ultraviolet spectra of $Cr(O_2PH_2)^{2+}$ and $Cr(O_3PH_2)^{2+}$ implies that the hypophosphite and hydrogenphosphite ions are very near each other in the spectrochemical series. The protonation of basic ligands coordinated to Cr(III) is invoked[5] to explain aquation kinetic terms, first-order in $[H^+]$, and Cr(III) complexes of ligands with protonated ammine sites uncoordinated to the metal ion are well known.[6] Protonation equilibria of cyanochromium(III)[7] and acetatochromium(III)[8] have been measured in strong-acid media; in both cases small decreases, similar to our findings, are observed in the visible molar absorptivities with increasing acidity. In the case of acetatochromium(III) an equilibrium quotient for the acid dissociation

$$Cr(OAcH)^{3+} \rightleftarrows Cr(OAc)^{2+} + H^+ \tag{2}$$

was found to be $Q_a(CrOAcH^{3+}) = 3.2$, at 25° and ionic strength 4 *M*, corresponding to an increase by a factor of 10^5 in the dissociation quotient of acetic acid on coordination to Cr^{3+}. For hydrocyanic acid the corresponding increase is by a factor of 10^8. The dissociation quotient of $Cr(O_3PH_2)^{2+}$ is only a factor of $10^{3.4}$ greater than that[9] of the hydrogenphosphite anion, $H_2PO_3^-$. The difference is perhaps attributable to the lower formal charge on the $-OPHO_2-$ moiety.

Aquation of $Cr(O_3PH_2)^{2+}$ is first order in $[H^+]$ as is that of $Cr(O_2PH_2)^{2+}$. The rate constant at 45°, k_H, 1.4×10^{-7} M^{-1} sec^{-1}, is lower than the corresponding k_H terms for other common mononegative basic ligands. In Table II are compiled k_H for a series of CrX^{2+} complexes and the corresponding pK_a for the neutral acid, HX.

TABLE II

ACID-DEPENDENT AQUATION OF CrX^{2+}

X^-	10^7k_H (CrX^{2+}, 45°), M^{-1} sec^{-1}	pK_a (HX, 25°)	X^-	10^7k_H (CrX^{2+}, 45°), M^{-1} sec^{-1}	pK_a (HX, 25°)
$H_2PO_2^-$	123[a]	1.3	N_3^-	140[d]	4.9
$H_2PO_3^-$	1.4[b]	2.0	CN^-	30,000[e]	8.7
F^-	2.0[c]	3.2			

[a] Reference 2. [b] This work. [c] T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965). [d] T. W. Swaddle and E. L. King, *ibid.*, **3**, 234 (1964). [e] J. P. Birk and J. H. Espenson, *ibid.*, **7**, 991 (1968).

The value of k_H decreases with decreasing pK_a except for the hypophosphito complex. For N_3^-, F^-, and CN^-, aquation necessarily proceeds with metal–ligand bond breaking. Espenson[10] has argued that the anomalously large rates of formation and aquation of the $Cr(O_2PH_2)^{2+}$ ion may be due to bond breaking at the P–O bond rather than Cr–O. If P–O bond breaking occurs in the aquation of $Cr(O_3PH_2)^{2+}$, it is evidently much slower than in the aquation of $Cr(O_2PH_2)^{2+}$. This

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is qualitatively supported by the results of ^{18}O-exchange studies between water and phosphorus acids; the first-order rate constants for exchange[11] decrease with increasing phosphorus oxidation state, $k(H_3PO_2) \gg k(H_3PO_3) \gg k(H_3PO_4)$. We anticipate that the acid-dependent aquation of the $Cr(O_4PH_2)^{2+}$ ion is even slower than that of $Cr(O_3PH_2)^{2+}$.

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The Fluorine-19 Nuclear Magnetic Resonance Spectrum of the Hexafluoroantimonate(V) Ion

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The ^{121}Sb and ^{123}Sb nmr spectra of the octahedral hexafluoroantimonate(V) ion in solutions of $NaSbF_6$ or SbF_5 in 48% aqueous hydrofluoric acid are known[2-4] to consist of seven-line multiplets due to spin–spin coupling of ^{19}F with the antimony nucleus. The corresponding multiplet structure expected for the ^{19}F nmr spectrum of this species, however, has apparently not been observed. We have now obtained complete resolution of this spectrum using a solution of the silver(I) salt in acetonitrile. The 14-line spectrum consists of a sextet arising from coupling of ^{121}Sb ($I = {}^5/_2$) with ^{19}F, superimposed on an octet due to coupling of ^{123}Sb ($I = {}^7/_2$) with ^{19}F. The spectrum is shown in the figure together with the corresponding ^{121}Sb and ^{123}Sb nmr spectra obtained in this laboratory. The coupling constants determined from the ^{19}F spectrum are $J_{\mathrm{F}-^{121}\mathrm{Sb}} = 1934\ (\pm 15)$ Hz and $J_{\mathrm{F}-^{123}\mathrm{Sb}} = 1047\ (\pm 25)$ Hz. The ratio $J_{\mathrm{F}-^{121}\mathrm{Sb}}/J_{\mathrm{F}-^{123}\mathrm{Sb}}$ is 1.85 ($\pm$0.06), in good agreement with the ratio of the gyromagnetic ratios $\gamma_{121}/\gamma_{123} = 1.8466$. The relative intensities of any two components due respectively to coupling with ^{121}Sb and ^{123}Sb is approximately 2:1, as expected for the isotopes in their natural abundances (^{121}Sb, 57.2%; ^{123}Sb, 42.8%). Although the symmetry of the intensity pattern is somewhat unsatisfactory (see Experimental Section), the overall line shape of the sextet is in qualitative agreement with that calculated by Suzuki and Kubo[5] for the nmr spectrum of a nucleus of spin $I = {}^1/_2$ coupled to a nucleus with spin $I = {}^5/_2$. The values of the coupling constants are in good agreement with those obtained from ^{121}Sb and ^{123}Sb nmr spectra by Hatton, *et al.* ($J_{\mathrm{F}-^{121}\mathrm{Sb}} = 1945\ (\pm 5)$ Hz; $J_{\mathrm{F}-^{123}\mathrm{Sb}} = 1055\ (\pm 5)$ Hz).[4,6] A value of $J_{\mathrm{F}-^{121}\mathrm{Sb}} = 1820$ Hz has also been determined from the ^{19}F nmr of solid $KSbF_6$.[7] The chemical shift of $AgSbF_6$ in acetonitrile, δ_{CFCl_3} +123 ppm, is within about 10 ppm of values found for absorptions previously assigned to SbF_6^-.[8-10]

Since ^{19}F nmr spectra previously reported for this ion have consisted of single absorptions with varying line widths, it was of interest to determine, qualitatively at least, the factors influencing resolution of the multiplet. For spin–spin coupling involving quadrupolar nuclei ($I > {}^1/_2$), the component line widths depend on the rate of quadrupole relaxation. Increase of either the electric field gradient around the high-spin nucleus or the rotational correlation time should increase the rate of relaxation and thus broaden the resonance lines.[11] For ionic species, the electric field gradient is expected to be sensitive to the magnitude of ion–ion interactions and hence to changes in dielectric constant (ϵ) of the solvent and change of the counterion. Previous studies of the ^{19}F nmr of the hexafluoroarsenate(V)[12] and -niobate(V)[13-15] ions have demonstrated the dependence of multiplet resolution on these factors.

We have found similar results for SbF_6^- in nonaqueous solution. The ^{19}F nmr of dilute solutions of $AgSbF_6$ in dimethyl sulfoxide ($\epsilon = 45.0$) and *N*,*N*-dimethylformamide ($\epsilon = 36.1$) showed resolution comparable to that for acetonitrile solution ($\epsilon = 38.0$), but noticeable broadening of the components occurred for dilute solutions in acetone ($\epsilon = 20.7$). The component line widths are also sensitive to change of cation. A solution of $NaSbF_6$ in acetonitrile, similar in concentration to that used to determine the ^{19}F spectrum of $AgSbF_6$ ($\sim$2 *M*), showed considerable broadening of both ^{19}F and ^{121}Sb multiplets. Saturated solutions of $AgSbF_6$ in dimethyl sulfoxide, *N*,*N*-dimethylformamide, and acetone were highly viscous and showed considerably broadened bands in their ^{19}F spectra, consistent with the increase in correlation time compared to dilute solutions. In the temperature range +50 to −40°, the ^{19}F spectra of the dilute solutions showed little change. The broad multiplets in the ^{19}F spectra of the viscous solutions, however, progressively coalesced to give somewhat sharper singlets as the temperature was lowered. The various line shapes were similar to those calculated by Suzuki, *et al.*[5] From these results, we conclude that, in nonaqueous solvents, multiplet resolution is mainly determined by solvent dependence of the rate of quadrupole relaxation.

Compared to their acetonitrile solutions, $AgSbF_6$ and $NaSbF_6$ in 48% aqueous hydrofluoric acid showed considerable broadening of the ^{19}F and ^{121}Sb multiplets.

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