assignment gives the best agreement with the analogy suggested by Table I, and it is also supported by the fact that Lide and Mann[3] found the e infrared band of perchloryl fluoride at 589 cm^{-1} to be more intense than the a_1 band at 549 cm^{-1}.

The infrared bands at 382.0 and 286 cm^{-1} have rather different contours, although both are assigned to species e. This is not surprising, because the Coriolis interactions commonly produce different band shapes for degenerate bands of the same species.

Table II lists and assigns all the observed bands of BrO_3F and the corresponding bands of ClO_3F. The seven combination bands observed in the infrared spectrum of BrO_3F can all be accounted for as overtones or binary sums.

In conclusion, the results of this study establish that perbromyl fluoride is isostructural with perchloryl fluoride; *i.e.*, it is a tetrahedral molecule of C_{3v} symmetry, with three oxygen atoms and one fluorine atom bonded to the central bromine atom.

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Spectroscopic and Chemical Properties of the Cyanotrihydroborate Anion

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The preparation of the potassium salt of the cyanotrihydroborate anion (KBH_3CN) is reported and a procedure for obtaining high-purity cyanotrihydroborate salts is outlined. The infrared and Raman spectra of BH_3CN^- and cyanotrideuterioborate (BD_3CN^-) are reported and the fundamental frequencies are assigned. The nmr and infrared data for this species are used to make qualitative comparisons of the bonding and structures of BH_3CN^- and other BH_3X adducts. The behavior of KBH_3CN in strongly acidic and neutral aqueous solutions is examined. K_b for hydrolysis of KBH_3CN is found to be approximately 10^{-10}. Attempted reductions of the cationic species Ag^+, Hg^{2+}, Cu^{2+}, and $Fe(CN)_6^{3-}$ by BH_3CN^- are discussed. A tentative mechanistic model for metal ion reduction is proposed and contrasted with that proposed for H^+.

Introduction

Several authors[2-9] have investigated BH_3 adducts in recent years. The interest in this area has ranged from investigations into the behavior of BH_3 as related to its isoelectronic analog O[3,4] to the general study of BH_3X compounds and attempts to correlate their chemical and structural properties.[2,5-8] Work in this latter area has been somewhat hampered by the lack of detailed information on a large number of BH_3X adducts. Recent reports by Parry and coworkers[3,4] and Keller[6] have contributed substantially to the available information on BH_3 adducts.

Wittig[10] first isolated BH_3CN^- as the lithium salt. His report gave limited solubility and stability data. More recent work by Borch[11] and others[12] has established the utility of $LiBH_3CN$ as a selective reducing agent for organic reductions. Also, Kreevoy[13] has published preliminary kinetic data for the acid (H^+) hydrolysis of $LiBH_3CN$ and proposed a mechanism for its decomposition. The possibility of coordination of BH_3CN^- by transition metal ions is obvious, but, to date, the only report on BH_3CN^-–M^+ complexes has been Shriver's[14] report that a solution of $Fe(phen)_2(CN_2)$ takes up B_2H_6. He found that the structure of the complexes formed from the metal cyanides was $M-CN-BH_3$. With BH_3CN^- the borane group is already carbon bound, and, if $M-CN-BH_3$ complexes are to form, linkage isomerization must take place. This possibility is intriguing and well worth our further investigation.

We wish to report, here, complete spectral data for BH_3CN^- and a brief discussion of some unusual properties of BH_3CN^-. Also, we use the spectral data to make qualitative comparisons between BH_3X adducts. Later reports will deal with the nature of the force field in BH_3CN^- and related molecules and give more complete data on several aspects of the transition metal chemistry of BH_3CN^-.

Experimental Section

Cation Exchange, Deuteration, and Purification Procedures for MBH_3CN and MBD_3CN Salts.—$LiBH_3CN$, purchased from Alfa Inorganics, was purified by precipitation of $LiBH_3CN \cdot$dioxane from ether solution.[10]

In a typical preparation of KBH_3CN, 0.10 mol of $LiBH_3CN \cdot$ dioxane in 50 ml of H_2O was added to 0.12 mol of $KF \cdot 2H_2O$ (Fisher Scientific) in 25 ml of H_2O. The resulting solution was cooled in an ice bath (0°) and the LiF precipitate was collected

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[1] NDEA Fellow, 1968–1969.

[2] V. D. Aftandilian, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **83**, 2471 (1961).

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[4] L. J. Malone and M. R. Manley, *ibid.*, **6**, 2260 (1967).

[5] B. Rice, R. J. Galiano, and W. J. Lehmann, *J. Phys. Chem.*, **61**, 1222 (1957).

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[7] H. Watanabe and K. Nagasawa, *ibid.*, **6**, 1068 (1967).

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[11] R. F. Borch and H. D. Durst, *J. Am. Chem. Soc.*, **91**, 3996 (1969).

[12] G. Drefahl and E. Keil, *J. Prakt. Chem.*, **6**, 80 (1958).

[13] M. M. Kreevoy and J. E. C. Hutchins, *J. Am. Chem. Soc.*, **91**, 4329 (1969).

[14] (a) D. F. Shriver, *ibid.*, **84**, 4610 (1962); (b) *ibid.*, **85**, 1405 (1963).

TABLE I[a]
INFRARED AND RAMAN SPECTRAL BANDS FOR MBH_3CN

ν, cm⁻¹						Ir ν, cm⁻¹		
Ir			Raman					
$LiBH_3CN$[b]	$NaBH_3CN$	KBH_3CN	KBH_3CN	Polarizn	Assignment	$NaBD_3CN$	KBD_3CN	Assignment
2385 m	2390 m	2390 m	2390 vw	p	$2\nu_6$	*2179 s*	*2179 s*	ν_1, $\nu^{a_1}_{CN}$
2350 sh	2350 sh	2350 sh	2352 sh	dp	$\nu_5(^{10}B)$, ν^{e}_{BH}	2100 vw	2100 vw	$\nu_5 - \nu_8$
2320 s	*2320 s*	*2320 s*	*2334 s*	dp	$\nu_5(^{11}B)$, ν^{e}_{BH}	1775 sh	n.o.	$\nu_5(^{10}B)$, ν^{e}_{BH}
2240 sh	2260 sh	2240 sh	2258 sh	p	$\nu_1(^{10}B)$, $\nu^{a_1}_{BH}$	*1760 s*	*1760 s*	$\nu_5(^{11}B)$, ν^{e}_{BH}
2220 m	*2240 m*	*2230 m*	*2239 m*	p	$\nu_1(^{11}B)$, $\nu^{a_1}_{BH}$	1700 w	1700 w	$\nu_6 + \nu_7$
2198 s	*2179 s*	*2179 s*	*2177 vs*	p	ν_2, $\nu^{a_1}_{CN}$	1670 sh	n.o.	$\nu_2(^{10}B)$, $\nu^{a_1}_{BH}$
n.o.	2120 vw	2125 vw	n.o.		$\nu(^{13}CN)$	*1660 m*	*1660 m*	$\nu_2(^{11}B)$, $\nu^{a_1}_{BH}$
2090 vw	n.o.	2075 vw	n.o.		$\nu_4 + \nu_6$	1255 vw	n.o.	$\nu_1 - \nu_3$
1200 m	*1195 m*	*1195 m*	*1195 m*	dp	ν_6, δ^{e}_{BH}			
n.o.	1145 sh	1137 sh	1136 sh	p	$\nu_3(^{10}B)$, $\delta^{a_1}_{BH}$	1050 m	1050 m	$\nu_5 - \nu_7$
1125[c] s	*1135 s*	*1128 s*	*1123 m*	p	$\nu_3(^{11}B)$, $\delta^{a_1}_{BH}$	940 sh	940 sh	$\nu_3(^{10}B)$, $\delta^{a_1}_{BH}$
1020 w	1020 w	1020 w	n.o.		$\nu_2 - \nu_3$	*920 s*	*920 s*	$\nu_3(^{11}B)$, $\delta^{a_1}_{BH}$
						875 w	*875 w*	ν_6, δ^{e}_{BH}
895[c] m	*890 w*	*890 w*	*888 vw*	...	ν_7, ρ^{e}_{BH}	*790 w*	*790 w*	ν_4, $\nu^{a_1}_{BC}$
870[c] m	*865 w*	*870 w*	*870 vw*	...	ν_4, $\nu^{a_1}_{BC}$	*675 w*	*675 w*	ν_7, ρ^{e}_{BH}
335 m	*358 m*	*360 m*	*358 w*	dp	ν^8, δ^{e}_{BCN}	*335 m*	*330 m*	ν_8, δ^{e}_{BCN}

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; v, very; p, polarized; dp, depolarized; n.o., not observed; ν, stretch; δ, bend; ρ, rock. [b] Dioxanate. [c] Approximate values due to overlapping dioxane bands.

on filter paper. The filtrate was evaporated on a Roto-vac at 25° and the solid was dried *in vacuo*. This precipitate was then dissolved in 10 ml of dry CH_3NO_2 (Fisher Certified) and filtered, and the nitromethane solution was poured into 100 ml of CCl_4 (Fisher Certified) with vigorous stirring. The white precipitate of KBH_3CN was collected on filter paper, washed several times with CCl_4, and dried *in vacuo*. The yield was approximately 75%. *Anal.* Calcd for KBH_3CN: B, 13.69; C, 15.21; N, 17.74; H, 3.83. Found: B, 13.42; C, 15.26; N, 17.73; H, 4.00.

$NaBH_3CN$ and $NaBD_3CN$ were supplied by Ventron Corp. and were recrystallized from CH_3NO_2 as described above.

In the preparation[13] of KBD_3CN, 0.5 g of KBH_3CN dissolved in 10 ml of D_2O was maintained at pH 2 ± 0.2 by addition of DCl for 1.5 hr. The D_2O was then evaporated on a Roto-vac at 25°. The resulting solid was recrystallized from CH_3NO_2. The yield was approximately 50% with 85–90% deuteration as estimated from the infrared spectrum.

Reaction of KBH_3CN with H^+.—Solutions (0.1 *M*) of KBH_3CN were decomposed by rapidly adding 0.4 *M* HCl on a standard vacuum line. The reaction was immediate and complete. The products were HCN, H_3BO_3, and H_2. Boric acid and hydrogen cyanide were identified by their infrared spectra while H_2 was identified as a noncondensable, flammable gas exhibiting no infrared spectrum.

The decomposition of BH_3CN^- in initially neutral water was also studied. KBH_3CN was added to pH 7 water in concentrations ranging from 10^{-3} to 0.3 *M* and gently stirred for 24 hr. The amount of decomposition, determined by collecting and measuring the total H_2 gas evolution, was found to be less than 0.5 mol % for all solutions. Infrared and pmr data show that BH_3CN^- is the only species detectable in these solutions after 24 hr.

Aqueous solutions of KBH_3CN, ranging from 0.08 to 0.16 *M*, were stirred for approximately 10 min and the pH was recorded with a Corning Model 7 pH meter equipped with Ag–AgCl and sce electrodes. A plot of pH *vs.* time showed that, as the KBH_3CN dissolved, the pH rose rapidly to a constant value (±0.2 pH unit) in less than 2 min and remained constant for over 10 min. It can be convincingly demonstrated from Kreevoy's rate data[13] that BH_3CN^- decomposition cannot account for the pH change over this interval of time. We therefore assumed that the observed pH change was due to protonation of the N atom and none was due to decomposition. This is further justified in view of the results of the decomposition studies. The average K_b for the reaction $BH_3CN^- + H_2O \rightleftharpoons BH_3CNH + OH^-$ was found to be $(2.1 \pm 2) \times 10^{-10}$.

Oxidation Studies.—Cyclic voltammetric studies were performed with a transistorized three-electrode potentiostat–galvanostat described previously[15] using 10^{-3} *M* aqueous solutions of KBH_3CN with 0.1 *M* KCl as the supporting electrolyte. The working electrode was a planar carbon paste electrode, the auxiliary electrode was made of platinum foil, and the reference electrode was a saturated calomel electrode (sce). The range scanned was +1.6 to −1.6 V, with no evidence of oxidation or raduction.

Chemical oxidations of KBH_3CN were carried out with 10^{-2} *M* solutions which were freshly prepared before each reaction. The reactions were followed spectrophotometrically in the cases of Cu^{2+} and $Fe(CN)_6^{3-}$. Metallic Ag and Hg were identified by their appearance and CuCN was identified by its infrared spectrum.

Redox Titration of KBH_3CN.—Solutions of I_2 (0.0906 *N*) and $S_2O_3^{2-}$ (0.1846 *N*) were prepared and standardized according to literature methods.[16] A 0.03408 *M* stock solution of KBH_3CN was also prepared. Excess I_2 was added to 10-ml aliquots of the KBH_3CN solution. After the reaction between KBH_3CN and I_2 had ceased, the excess I_2 was titrated with standard $S_2O_3^{2-}$. The equivalent weight of KBH_3CN was found to be 10.605 ± 0.0023. This corresponds to a six-electron change within experimental error. A half-cell reaction consistent with these data is $BH_3CN^- + 3H_2O \rightarrow B(OH)_3 + CN^- + 6H^+ + 6e^-$.

Spectroscopic Measurements.—Nmr spectra were recorded on a Varian A-60 spectrometer using D_2O as solvent and impurity H_2O reference. All visible and ultraviolet spectra were scanned with a Cary Model 14 spectrophotometer. Infrared spectra, in the range 4000–250 cm^{-1}, were recorded on a Perkin-Elmer 457 grating spectrometer from KBr pellets and Nujol mulls. Raman data were obtained on a Spex Industries Model 1400 double-grating spectrometer equipped with an He–Ne source using polycrystalline samples and 2 *M* aqueous solutions. Polarization data were taken from the aqueous solutions.

Elemental Analyses.—All analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Results

Table I lists the observed infrared bands for KBH_3CN, $NaBH_3CN$, and $LiBH_3CN \cdot$dioxane and, in addition, the Raman bands for KBH_3CN. The band assign-

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(15) J. C. Lawless and M. D. Hawley, *J. Electroanal. Chem.*, **21**, 365 (1969).

(16) A. H. Ayres, "Quantitative Chemical Analysis," Harper and Brothers Inc., New York, N. Y., 1958.

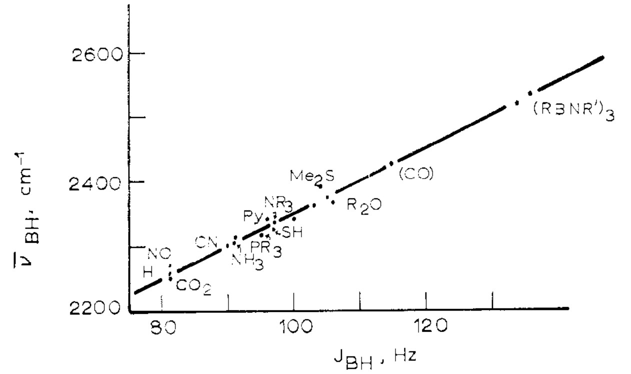


Figure 1.—ν_{BH}^{av} *vs.* $J_{^{11}BH}$. Note: $J_{^{11}BH}$ is not available for BH_3CO; ν_{BH}^{av} is plotted merely for reference.

ments have been made with the aid of the Raman polarization data and are consistent with assignments which have been made[2,5,17,18] for a large number of BH_3X compounds. The infrared bands listed for $LiBH_3CN$ are those frequencies which cannot be attributed to dioxane.

The E and A_1 BH stretching and bending vibrations are fairly easily assigned by comparison with other BH_3X molecules and from the polarization data. The CN stretch is observed as a sharp peak characteristic of cyanide bands. The position of the CN stretch at 2179 cm^{-1} is intermediate[19] between that of ionic cyanide (2080 cm^{-1}) and covalently bound cyanide such as reported for the isoelectronic molecule CH_3CN (2267 cm^{-1}). None of our spectra revealed a band in this region which could be assigned to the linkage isomer BH_3NC^-.[20] The two bands most difficult to assign are the BC stretch and the BH_3 rock, ν_4 and ν_7, respectively. Unfortunately, the polarization data obtained from the Raman spectrum do not allow an unambiguous assignment of these bands, even though the two associated vibrational modes are of different symmetry. The weak Raman scattering of these two bands has thus far prevented us from obtaining accurate polarization data. The assignment of ν_4 to the 870-cm^{-1} band and ν_7 to the band at 890 cm^{-1} is that most consistent with all available data. Furthermore, this assignment gives excellent agreement for the Teller–Redlich product rule. Details of the assignment difficulties and unusual isotope effects will accompany a future report on the force field for BH_3CN^-.

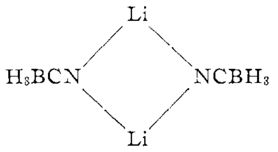
The spectral bands of the deuterated sodium and potassium salts are recorded in Table I. The frequencies listed are those which are not assignable to absorptions from the small amount of normal compound present because of incomplete H–D exchange. The fundamentals of the deuterated species are assigned in a manner similar to that used for the normal isotopic compound, with the constraint of the Teller–Redlich product rule.

The proton nmr spectrum of KBH_3CN in D_2O consists of a sharp and well-resolved quartet and septet which arise from coupling of the protons with ^{11}B ($I = {}^3/_2$) and ^{10}B ($I = 3$) nuclei, respectively: $J_{^{11}BH} =$ 90 Hz and $J_{^{10}BH} = 30$ Hz. The coupling constant ratio of 3 is that expected on the basis of the magnetogyric ratios[21] for ^{11}B and ^{10}B. The centers of the proton multiplets coincide at 252 Hz upfield from the impurity H_2O resonance signal.

The visible and ultraviolet regions of the spectrum were scanned using aqueous soluions, but no electronic absorption maxima were observed between 700 and 200 mμ. The absence of absorption maxima in this region is typical for cyano compounds. Acetonitrile exhibits an electronic transition at approximately 180 mμ which tails beyond 200 mμ. We found a similar tail for the aqueous solution spectrum of BH_3CN^-.

Discussion

One unexpected result of a comparison of the infrared data for the Li^+, Na^+, and K^+ salts is the rather large shifts in ν_2 and ν_8 observed for $LiBH_3CN \cdot$dioxane. The high-energy shift in the CN stretch (ν_2) is particularly significant since ν_{CN} does not change upon deuteration. We believe these shifts are due to an interaction between Li^+ and the nitrogen atom of the anion. Unpublished X-ray data[22] indicate that the lithium ions (in the nonsolvated salt) are equidistant from and coplanar with the N atoms, *i.e.*, local D_{2h} symmetry



This dimeric structure could account for the shift of ν_2 and ν_8 on exchanging Li^+ for Na^+ or K^+. While splitting of ν_8 might be expected, none was observed. An alternative explanation, that the shifts are due to a BH_3CN^-–dioxane interaction, is less satisfactory because ν_2 and ν_8 in $NaBH_3CN \cdot$dioxane are unshifted from their positions in $NaBH_3CN$. Furthermore, spectra of $LiBH_3CN$ in ether exhibit the same shifts of ν_2 and ν_8 as observed in the solid-state spectra (the salt is most certainly ion-paired in ether).

In 1957, Rice[5] discussed a correlation between ν_{BH}^{sym} and stability for a series of BH_3X compounds. Other authors[8,23,24] have commented on the relationship between J_{BH} and the boron "s" character in the boron hydrogen bond. More recently, Watanabe[7] has discussed the linear relationship between the weighted average of ν_{BH} and $J_{^{11}BH}$ for an extensive series of boron compounds. We have plotted (Figure 1) ν_{BH}^{av} *vs.* $J_{^{11}BH}$ for a series of BH_3X molecules and have found

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(17) S. Sundaram and F. F. Cleveland, *J. Chem. Phys.*, **32**, 166 (1960).

(18) B. Rice and H. S. Uchida, *J. Phys. Chem.*, **59**, 650 (1955).

(19) K. F. Purcell, *J. Am. Chem. Soc.*, **89**, 6139 (1967).

(20) (a) R. T. Holzmann, M.S. Thesis, University of Delaware, 1955. (b) The possibility that either of the two weak bands at 2125 or 2075 cm^{-1} could be due to BH_3NC^- was considered. However, we believe the correct assignment to be that listed in Table I, because in a preliminary study of a sample of $NaBH_3NC$ we observed ν_{NC} at 2065 cm^{-1}.

(21) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

(22) W. C. Baird, private communication.

(23) H. S. Gutowsky, O. W. McCall, and C. P. Slichter, *J. Am. Chem. Soc.*, **75**, 4567 (1953).

(24) T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

that the linear $\nu_{BH}{}^{av}$–J_{BH} correlation is even better when limited to data for borane adducts. It is possible to use this correlation to infer qualitative features of the BX bonding and to assess the stability of the adducts.

The limiting hybridization schemes in Figure 1 are sp^3, represented by data for BH_4^-, and sp^2 represented by $H_3N_3B_3H_3$. According to Bent's isovalent hybridization arguments,[25] the B–H bond strength will be proportional to the boron "s" character in those bonds. To the extent that the BH stretching frequencies adequately reflect the BH force constants and J_{BH} adequately represents the boron "s" character in the BH bonds, Bent's concept of increasing force constant with increasing "s" character is nicely borne out for the series in Figure 1.

The electron-withdrawing character of CN relative to H has been invoked[10,13] to account for the pronounced stability, in aqueous acid, of BH_3CN^- relative to BH_4^- since the intermediate in both cases is proposed[13] to be BH_4X. This comparison can be extended to BH_3CO. The BH_3CO analogy is especially interesting since it is known that BH_3CO decomposes by two mechanisms.[3,4] One mechanism involves solvation of BH_3CO by H_2O to form $BH_3C(OH)_2$ which decomposes to $(HO)_2BCH_2OH$; the other mechanism involves SN1 dissociation to BH_3 and CO and yields $B(OH)_3$ upon decomposition. The important point here is that attack of H^+ at the BH_3 moiety does not appear[3] to be very important in the decomposition of BH_3CO, and this is consistent with the expected electron-withdrawing capability of CO, relative to CN and H. H charge densities, as computed by the CNDO/2[26] method, also support these conclusions inasmuch as the BH_4^- hydrogens carry considerably more negative charge (−0.20) than do those of the CN^- (−0.15) and especially the CO (−0.02) adducts.

It is also interesting to compare the adduct bond strengths of the carbon donors CO_2^{2-}, CN^-, and CO on the basis of their respective adduct bond stretching motions. When qualitatively estimating bond strengths from vibrational data, force constants are more satisfactory than frequencies; however, in the absence of complete force constant data, frequency comparisons can be useful if applied carefully. From Figure 1 we see that BH_3CO is closer to the sp^2 limit than either $BH_3CO_2^{2-}$ or BH_3CN^- and therefore is expected, on the basis of isovalent hybridization arguments, to have the weaker B–C bond. The B–C stretching frequencies in Table II support this expectation as ν_{BC} for BH_3CO is ~150 cm^{-1} lower than ν_{BC} for $BH_3CO_2^{2-}$ or BH_3CN^-. Also in agreement with the relative positions of BH_3CN^- and BH_3CO in Figure 1, a CNDO/2 calculation, the results of which will be discussed in more detail later, shows that B utilizes about 7% more "s" character in binding CN^- than CO.

TABLE II

COMPARISON OF FUNDAMENTAL VIBRATIONS (CM^{-1})

BH_3CN^-	BH_3CO[c]	$BH_3CO_2^{2-}$[a]	Assignment[b]	BD_3CN^-	BD_3CO[c]
2320	2434	2275	$\nu^e{}_{BH}$	1760	1837
2230	2380	2226	$\nu^{a_1}{}_{BH}$	1660	1679
2179	2169		$\nu^{a_1}{}_{CN,CO}$	2179	2169
1195	1101	1193	$\delta^e{}_{BH}$	875	801
1128	1073	1150	$\delta^{a_1}{}_{BH}$	920	862
890	816	900	$\rho^e{}_{BH}$	675	709
870	692	855	$\nu^{a_1}{}_{BC}$	790	625
360	317		$\delta^e{}_{BCN}$	330	266

[a] Reference 3. [b] Symbols: ν, stretch; δ, bend; ρ, rock. [c] Reference 17.

A more general extension of the above comparisons to include the other molecules of the BH_3X type would be useful; however, some caution is necessary when comparing the stability of adducts with different donor atoms. For example, Rice[5] noted that the relationship between $\nu_{BH}{}^{sym}$ and stability did not hold for the $(CH_3)_2O$ ($K_p = \infty$, 20°) and $(CH_3)_2S$ ($K_p = 0.894$, 60°) borane adducts. The relative $\nu_{BH}{}^{sym}$ values predict that $(CH_3)_2SBH_3$ is less stable than $(CH_3)_2OBH_3$. He proposed that B–S π bonding might account for the unusual stability of $(CH_3)_2SBH_3$. The coupling constant data, Table III, for these two adducts indicate that the sulfur adduct is the more stable, *i.e.*, more boron "s" character in the B–S bond. Furthermore, force constants[5] calculated for the B–X bond, using a BH_3X model, yield the same order of stabilities for these two adducts as do the K_p's and the J_{BH}'s. It therefore seems reasonable to attribute the discrepancy in $\nu_{BH}{}^{sym}$ to an anomalous BH stretching frequency, perhaps arising from Fermi resonance[5,18] between ν_1 and $2\nu_3$, and it is not necessary to invoke B–S π bonding to explain the unusually large $\nu_{BH}{}^{sym}$ for $(CH_3)_2SBH_3$.

TABLE III

INFRARED AND NMR DATA FOR BH_3X

Species	$J_{^{11}BH}$, Hz	$\nu_{BH}{}^{av}$, cm^{-1}
BH_3–H^-	80[a]	2245[b]
BH_3–CO_2^{2-}	81[3]	2251[3]
BH_3–NO^-	81[c]	2268[c]
BH_3–CN^-	90	2293
BH_3–NH_3	91[a]	2306[d]
BH_3–$PH_2(BH_3)^-$	91[c]	2312[c]
BH_3–$P(CH_3)_3$	95[e]	2323[f]
BH_3–NC_5H_5	96[a]	2339[5]
BH_3–SH^-	97[b]	2323[6]
BH_3–$N(CH_3)_3$	97[a]	2337[5]
BH_3–$N(C_2H_5)_3$	97[a]	2340[5]
BH_3–$PH_2(CH_3)$	100[c]	2340[e]
BH_3–C_4H_8O	103[a]	2360[18]
BH_3–$(CH_3)_2S$	104[a]	2385[5]
BH_3–$(CH_3)_2O$	106[a]	2365[18]
BH_3–CO	n.a.[g]	2421[17]

[a] H. Steinburg and A. L. McCloskey, *Progr. Boron Chem.*, **1**, 453 (1964). [b] A. R. Emery and F. C. Taylor, *J. Chem. Phys.*, **28**, 1029 (1958). [c] J. W. Gilje, Ph.D. Thesis, University of Michigan, 1965. [d] J. Goubeau, *Z. Anorg. Allgem. Chem.*, **310**, 123 (1961). [e] J. G. Verkade, R. W. King, and C. W. Heitsch, *Inorg. Chem.*, **3**, 884 (1964). [f] L. Banford and G. E. Coates, *J. Chem. Soc., A*, 274 (1966). [g] n.a., not available.

The sharpness of the proton nmr signal of BH_3CN^- is also significant. Nuclear quadrupole broadening of the proton resonance line will result from an electrical field

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(25) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

(26) Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind.

gradient at the quadrupolar boron nucleus.[27] The proton nmr spectrum clearly indicates a high electric field symmetry at the boron nucleus. CNDO/2 calculations support this statement in that the computed B "excess p_z density" is very small: ~0.0 for BH_3CN^- which can be compared with −0.2 for BH_3CO. This absence of quadrupolar broadening is also observed with $BH_3CO_2^{2-}$.[3] The sharp BH_3 quartet is also consistent with the infrared results in that no linkage isomer, BH_3NC^-, could be detected in our samples. It has been reported[28] that isonitriles exhibit an unusually small electric field gradient at nitrogen which permits resolution of the N–H coupling. We observed no splitting or broadening which could be attributed to N–H coupling.

In 12 N HCl, KBH_3CN rapidly hydrolyzes

$$BH_3CN^- + 3H_2O + HCl \longrightarrow H_3BO_3 + HCN + 3H_2 + Cl^-$$

In initially neutral aqueous solutions, BH_3CN^- hydrolysis is very slow (<0.5% in 24 hr). Addition of even a small amount of acid (0.016 mmol of H^+ to 4.1 mmol of BH_3CN^- in 40 ml H_2O) at room temperature will induce decomposition as evidenced by very erratic pH readings. However, if a similar aqueous solution is cooled to 0°, the same amount of acid will cause no immediate decomposition and the pH readings are stable over a 30-min period. At 0°, a 0.1 M solution of BH_3CN^- behaves very nearly as pure water on addition of H^+, indicating that BH_3CN^- behaves as a very weak base toward the proton.

Since KBH_3CN is too weak as a base to titrate in aqueous solution, we have approximated K_b by measuring the pH of aqueous solutions at various concentrations. It might be reasoned that decomposition of BH_3CN^- could lead to the observed pH change, since one of the products, CN^-, will be extensively hydrolyzed in solution. This possibility was considered but discarded because published rate data,[13] as well as our own studies, have shown that in the time necessary to measure the pH (<3 min) the decomposition reaction is completely negligible. From our data, K_b is estimated to be approximately 10^{-10}. Parry[3] has reported similar data for $BH_3CO_2^{2-}$; he found $K_1 \approx 10^{-8}$ and $K_2 \approx 10^{-11}$.

Also, when compared to the isoelectronic analog CH_3CN, the basicity of BH_3CN^- toward the proton is not surprising. Acetonitrile is known to behave as a very weak base toward the proton, as it cannot be titrated even in acetic acid.[29] Replacement of CH_3^+ with BH_3 is expected to increase the basicity of the N lone pair, making KBH_3CN a slightly better base than CH_3CN.

The redox chemistry of BH_3CN^- is interesting. Silver(I) and mercury(II) are stronger oxidants than H^+ and they are rapidly reduced by aqueous BH_3CN^-. Coordination of Ag^+ and Hg^{2+} by BH_3CN^- is an obvious mechanistic possibility; however, such coordination is also possible for H^+, yet the rate of BH_3CN^- oxidation is dramatically less for H^+ ($t_{1/2} \approx 2$ hr at pH 2[13]) than for Ag^+ and Hg^{2+} (essentially diffusion controlled). This suggests that the H^+ oxidation occurs by an entirely different mechanism, *e.g.*, that proposed by Kreevoy.[13] That coordination of BH_3CN^- by Ag^+ is a prerequisite for the redox reaction is indicated by the fact that ammoniacal solutions of Ag^+ are considerably stabilized ($t_{1/2} \approx 30$ min). When neutral solutions of Ag^+ are added to a solution of BH_3CN^-, a white precipitate forms which rapidly deposits silver. Attempts to isolate the precipitate have been unsuccessful. We can surmise that insoluble $AgBH_3CN$ forms initially and subsequently undergoes rapid decomposition. It is important to note that the oxidation half-reaction of BH_3CN^- does not require H^+; *i.e.*

$$BH_3CN^- + 3H_2O \longrightarrow B(OH)_3 + 6H^+ + CN^- + 6e^-$$

This is important in explaining the slowness with which BH_3CN^- reduces the silver diammine complex; *i.e.*, the basic conditions will not inhibit the reaction—except that NH_3 impedes the "inner-sphere" coordination by BH_3CN^-, which is apparently necessary for metal ion oxidation of BH_3CN^-, or the presence of coordinated NH_3 in a mixed-ligand complex stabilizes the metal ion to reduction.

Similarly, aqueous Cu^{2+} is reduced by BH_3CN^-. We find the rate of this reaction to be intermediate between those of Ag^+ and Hg^{2+} on one hand and H^+ on the other. The initially blue Cu^{2+} solution (λ_{max} ~680 mμ) slowly changes to a green solution (λ_{max} ~525 mμ), followed by precipitation of CuCN in about 10 min. If excess BH_3CN^- is present, the white CuCN precipitate will, in about 4 hr, be reduced to Cu^0. On the other hand, Cu^{2+} in ammoniacal solution appears to be stable for extended periods of time. Again, it appears that BH_3CN^- must coordinate Cu^{2+} to effect reduction. In addition, we find the rate of Cu^{2+} reduction to be anion dependent. $Cu(NO_3)_2$ solutions take about 10 min for formation of CuCN while $CuCl_2$ solutions require over 30 min for the formation of CuCN.

Thus it appears that anion coordination (assumed to be more important for Cl^- than for NO_3^-) inhibits the reduction of Cu^{2+} in much the same manner as NH_3 inhibits the reduction of Ag^+ and Cu^{2+}. Taking into account the lability of chloro complexes, a likely possibility is that mixed $Cl–BH_3CN^-$ complexes are formed which are more stable than mixed $H_2O–BH_3CN^-$ complexes. A similar situation appears to occur with the phenanthroline complexes.[14]

Finally, a ferricyanide solution ($Fe(CN)_6^{3-}$ is a better oxidant than Cu^{2+}) was added to a BH_3CN^- solution and no reaction was observed. The stability of the ferricyanide complex ($K_d = 10^{-31}$) apparently inhibits the replacement of CN^- by BH_3CN^- and thus prevents reduction of ferricyanide to ferrocyanide. These data,

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as well as the failure to observe electrochemical oxidation, consistently suggest that inner-sphere coordination is necessary for reduction. Therefore, in accepting Kreevoy's proposed mechanism for the proton, we conclude that the mechanisms for reduction are different for proton and metal ions. Further work in this area is underway in an attempt to elucidate the exact nature of the metal ion reactions and their mechanisms.

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Metal Complexes of the Difluorodithiophosphate Ligand

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Difluorodithiophosphato, $F_2PS_2^-$, derivatives of monovalent Cu, Ag, and Au, divalent Mn, Fe, Co, Ni, Pd, Pt, Zn, Cd, and Hg, and trivalent Cr, Co, and Rh have been isolated and characterized. Many of these transition metal complexes are extremely volatile as exemplified by the Co(II) derivative which has a vapor pressure of 20 mm at 95°. In contrast, the silver and copper(I) derivatives are nonvolatile and may have polymeric structures. All the difluorodithiophosphato complexes are susceptible to hydrolysis, but the rates vary widely from low in chromium(III) and nickel(II) to high in many of the bis derivatives. Chemically, the bis derivatives are the most reactive set and complex with donor molecules such as water, acetonitrile, phosphines, and anions. In this manner $R_3PPd(S_2PF_2)_2$, $R_3AsPd(S_2PF_2)_2$, $(R_3P)_2Pd(S_2PF_2)_2$, and $Pd(S_2PF_2)_3^-$ have been isolated. These palladium complexes are believed to have square-planar form. Nitric oxide reacts with the bis derivatives of iron and cobalt to give the unusual nitrosyls $(ON)_2MS_2PF_2$.

Introduction

Through reactions of tetraphosphorus decasulfide a series of novel anions of the type $X_2PS_2^-$ was prepared.[1,2] Of primary interest to us has been the transition metal derivative chemistry of these anions, and there is a preliminary account of the $F_2PS_2^-$ system.[3] Later, several difluorodithiophosphatometal carbonyls, *e.g.*, $[Rh(CO)_2(S_2PF_2)]_2$, were reported.[4] Herein are reported the details of our transition metal studies with the difluorodithiophosphate anion.

Results and Discussion

Synthesis.—Complexes of the more electropositive metals were prepared by simply stirring the anhydrous acid HS_2PF_2 with finely divided metal. In this manner, the tris derivative of chromium, the mono derivative of copper, and the bis derivatives of manganese, iron, cobalt, nickel, zinc, and cadmium were obtained. Chloride displacement from the chlorides of palladium(II), platinum(II), rhodium(III), and triphenylphosphinegold(I) with HS_2PF_2 yielded the respective crystalline complexes with the metals in unaltered valence states. The silver derivative was prepared by neutralization of silver oxide with the acid. The cobalt(III) and iron(III) complexes were obtained by the oxidation of the divalent derivatives with air or $(F_2PS_2)_2$.[2] The latter reagent was employed to oxidize mercury to $Hg(S_2PF_2)_2$.

Spectral Data.—Spectral data are presented here in general outline to facilitate later discussions of structure for the difluorodithiophosphato complexes. Fluorine nmr spectra were obtained for diamagnetic and the paramagnetic $Cr(S_2PF_2)_3$ and $Co(S_2PF_2)_2$ complexes. Spectra of the paramagnetic species consisted of broad structureless resonances. Diamagnetic species generally produced simple sharp doublets arising from P–F coupling on the order of 1200–1300 Hz. Fine structure in the spectrum of $Co(S_2PF_2)_3$ (Figure 1) apparently reflects $^{59}Co-^{19}F$ coupling. Platinum–fluorine coupling is apparent in the spectrum of $Pt(S_2PF_2)_2$. This and the spectrum of $Pd(S_2PF_2)_2$ contain additional structure arising from long-range phosphorus or fluorine coupling. The magnitudes of P–F coupling constants for derivatives of $F_2PS_2^-$ were sensitive to the environment of the group, and most of the values were clustered around one of three numbers. The lowest value encountered was 1158 Hz for the anion as a tetraalkylammonium salt. Coordination of the group through one or both of the sulfur atoms resulted in an increase of the coupling constant. Several compounds of reasonably certain structure such as $C_2H_5SP(S)F_2$ and HS_2PF_2[1,2] have coupling constants in the neighborhood of 1200 Hz. In addition several species of unknown structure such as complexes of the copper and zinc triads have coupling

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