92% ^{10}B. The samples were prepared by Dr. Patty Clippard using standard preparations.[6]

Results and Discussion

Since the boron and the nitrogen atoms lie on the symmetry axis, the B–N distance could be evaluated reliably even though the structure of the remainder of the molecule was not determined. The coordinates of the nitrogen and boron were calculated by the substitution method using Kraitchman's equations.[7] The coordinates obtained for the boron and the nitrogen, respectively, were $|0.7761|$ and $|0.8599|$ Å. These resulted in a B–N bond distance of 1.636 ± 0.004 Å. The uncertainty is associated with the experimental uncertainty in the frequency measurements.

The B–N distance determined here is somewhat longer than that determined from the X-ray analysis from which Geller and Hoard[8] reported a value of 1.585 ± 0.03 Å. It is difficult to ascertain whether this difference unequivocally indicates a change in the B–N bond length between the gas and the solid. Geller and Hoard pointed out in their report that their structure determination was inferior to that normally obtained by X-ray diffraction.

A recent crystallographic study in this department of some boron trihalide complexes of trimethylamine resulted in the following B–N bond distances:[9] $(CH_3)_3N \cdot BCl_3$,[10] 1.610 ± 0.006 Å; $(CH_3)_3N \cdot BBr_3$, 1.603 ± 0.02 Å; $(CH_3)_3N \cdot BI_3$, 1.584 ± 0.025 Å. Although the uncertainties in the values for the bromo and the iodo complexes are rather large, there appears to be a small decrease in the bond lengths in the series. The 1.636 ± 0.004 Å distance for the fluoro complex correlates quite smoothly with this trend. It is interesting to note that this decrease is consistent with the results of various dipole moment,[11] calorimetric,[12] and displacement[13] studies on the acceptor power of the boron trihalides toward trimethylamine.

The structure of trimethylamine–borane has been obtained from the analysis of the microwave spectra of eight isotopic species.[3] A value of 1.65 ± 0.02 Å was obtained for the B–N distance which is comparable to that of the fluoro complex. The results of several stability studies indicate that the acceptor strengths of boron trifluoride and borane toward trimethylamine are approximately the same.[4] Therefore, similar B–N bond distances would be expected for $(CH_3)_3N \cdot BH_3$ and $(CH_3)_3N \cdot BF_3$.

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Basicity of Nitrogen Trifluoride in the Gas Phase by Ion Cyclotron Resonance

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The study of acid–base phenomena deservedly remains an important area of endeavor in chemistry. The determination of acidities and basicities of molecules in the gas phase is especially valuable because complicating effects of solvation phenomena are avoided.[3-7] The new technique of ion cyclotron resonance spectroscopy (icr) is especially suited for the determination of gas-phase thermochemical quantities such as the acidity and basicity of molecules.[4-7] In contrast to ammonia, nitrogen trifluoride, NF_3, has been described as completely lacking in basic properties.[8] We report here the quantitative determination of the gas-phase proton affinity (basicity) of NF_3 based on the observation by icr of the course of ion–molecule reactions occurring in binary mixtures of NF_3 with CH_4 and HCl.

Experimental Section

The instrumentation and experimental techniques associated with ion cyclotron resonance spectroscopy have been previously described in detail.[6] Commercial samples of NF_3 (Air Products), CH_4 (Matheson), and HCl (Baker) were subjected to repetitive freeze–pump–thaw cycles before use.

Results

The ion chemistry of NF_3 alone and in binary mixtures with CH_4 and HCl was examined between 10^{-7} and 10^{-3} Torr at 70 eV. Nitrogen trifluoride chemically attacks the rhodium-plated metal surfaces of the icr cell and filament wire, making pressure studies difficult. It was found necessary to change the icr cell drift and trapping voltages with nearly every scan. Such operating conditions make impossible the extraction of reaction rate constants for processes observed. However, it was still possible to monitor the course of reaction by pressure variation and icr double-resonance experiments.

Nitrogen Trifluoride.—The icr single-resonance spectrum at 10^{-7} Torr was in agreement with the known

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mass spectrum of NF_3.[9,10] As the NF_3 pressure is raised, ion–molecule reactions occur to deplete NF^+ and N^+ with a concomitant increase in the formation of NF_2^+. Both NF_2^+ and NF_3^+ are unreactive toward NF_3 between 10^{-7} and 3×10^{-4} Torr, the highest pressure observed.

Nitrogen Trifluoride and Methane.—A 1:2.3 mixture of NF_3 and CH_4 was examined between 10^{-6} and 2×10^{-3} Torr. Besides ions observed for the pure components alone,[11] a new ion, protonated nitrogen trifluoride, NF_3H^+, is observed. Pressure dependence of single-resonance intensities as well as double-resonance experiments reveal the occurrence of reaction 1 and the nonoccurrence of reaction 2.

$$CH_5^+ + NF_3 \longrightarrow NF_3H^+ + CH_4 \qquad (1)$$

$$C_2H_5^+ + NF_3 \not\longrightarrow NF_3H^+ + C_2H_4 \qquad (2)$$

Nitrogen Trifluoride and Hydrogen Chloride.—A 2.5:1 mixture of NF_3 and HCl was examined between 10^{-6} and 2×10^{-4} Torr. Besides ions observed for the pure components alone, a new ion, protonated nitrogen trifluoride, NF_3H^+, is observed. Pressure dependence of single-resonance intensities as well as double-resonance experiments indicates that reaction 3 proceeds to the right.

$$H_2Cl^+ + NF_3 \longrightarrow NF_3H^+ + HCl \qquad (3)$$

Discussion

The only ion–molecule reaction of note observed in binary mixtures of NF_3 with CH_4 and HCl is the formation of the protonated molecule NF_3H^+. Important thermochemical deductions are possible, however. The enthalpy change for the gas-phase reaction $MH^+ \rightarrow M + H^+$ is known as the proton affinity (PA) of the species M and is a quantitative measure of the basicity of M.[3-6] Since gas-phase ion–molecule reactions are assumed to proceed with negligible activation energy,[12-15] the observation of a process such as reaction 4 is usually interpreted as indicating that $PA(M_2) \geq PA(M_1)$. Thus from reactions 1–3 reported above and

$$M_1H^+ + M_2 \longrightarrow M_2H^+ + M_1 \qquad (4)$$

the known values of $PA(CH_4)$ = 126 kcal/mol,[3] PA(HCl) = 141 kcal/mol,[3] and $PA(C_2H_4)$ = 160 kcal/mol,[16] an estimate of $PA(NF_3)$ = 151 ± 10 kcal/mol is derived, corresponding to $\Delta H_f(NF_3H^+)$ = 185 ± 10 kcal/mol.

The proton affinity of NF_3 is 56 kcal/mol less than that of NH_3,[3] a difference corresponding to 40 p*K* units at 25°. In the absence of solvation effects, NF_3H^+ would be estimated to have $pK_a = -31$ in aqueous solution. Hall[17] has shown that the base strengths in aqueous solution of tertiary aliphatic amines are adequately correlated by means of the linear free energy relationship given in eq 5 with $\rho^* = -3.30$. Coupled with the σ^* value of 3.08 given by Taft[18] for fluorine, the estimated aqueous pK_a of NF_3H^+ is calculated to be −21. In agreement with both estimates, Gillespie and Pez[19] have found that NF_3 does not protonate in $HSO_3F–SbF_5$, indicating $pK_a \leq -16$.

$$\log (K/K_0) = \rho^* \Sigma \sigma^* \qquad (5)$$

The present work allows the calculation of some interesting thermochemical quantities which separate the various factors contributing to the difference in basicities of NF_3 and NH_3. The proton and hydrogen affinities of a molecule and its corresponding ion are interrelated by ionization potentials as shown in eq 6.[4,5]

$$PA(M) - HA(M^+) = IP(H) - IP(M) \qquad (6)$$

The hydrogen affinity, $HA(M^+)$, is simply the $H–M^+$ bond strength $D(H–M^+)$. A summary of hydrogen affinities and bond strengths for isoelectronic species is presented in Table I. As expected, the M–H bond strength increases in proceeding to the isoelectronic ion; the increase of 20–30 kcal/mol has been noted previously in other systems.[5] However, both the hydrogen affinity $D(H–NH_3^+)$ and the bond strength in the isoelectronic neutral $D(H–CH_3)$ remain approximately constant when three fluorines are substituted for hydrogens in NH_3 and CH_4. Thus, while the proton affinities (basicities) of NF_3 and NH_3 differ greatly, the N–H bonds in NF_3H^+ and NH_4^+ are similar. This phenomenon of the constancy of the hydrogen affinity with substituent changes appears to be general for many other types of molecules, for example, alcohols,[20] ethers,[20] aldehydes,[20] ketones,[20] and alkyl halides.[20,21] *Thus, basicity differences for many series of functionally similar molecules are given to good quantitative approximation simply by differences in ionization potential.* As required by eq 6, the correlation of basicities with ionization potential becomes exact whenever hydrogen affinities are invariant to substituent changes.

TABLE I

BOND STRENGTHS OF SOME ISOELECTRONIC SPECIES[a]

Ion	Hydrogen affinity[b]	Neutral	M–H bond energy[c]
NF_3H^+	138 ± 10	CF_3H	106
NH_4^+	128 ± 3	CH_4	104

[a] All values in kilocalories per mole. [b] $HA(M^+)$ from eq 6; $PA(NF_3)$ = 151 kcal/mol (see text); $IP(NF_3)$ = 300 kcal/mol (V. H. Dibeler and J. A. Walker, *Inorg. Chem.*, **8**, 1728 (1969)); $PA(NH_3)$ = 207 kcal/mol;[3] $IP(NH_3)$ = 234 kcal/mol;[16] $IP(H\cdot)$ = 313 kcal/mol.[16] [c] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

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The Synthesis of μ-Isocyano-pentacyano-pentaamminedicobalt(III)[1a,b]

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Linkage isomerism for terminal and bridging cyanide groups bound to transition metal ions has been reported in recent years. For terminal cyanide groups, the nitrogen-bonded isomers have been detected as metastable intermediates in inner-sphere redox reactions and are known to undergo relatively rapid isomerization to the stable carbon-bonded structures.[2-4] In the case of bridging cyanide groups, linkage isomerism has been reported for the ill-defined, polymeric materials that precipitate on mixing transition metal–aquo ions with transition metal hexacyanides.[5-7] We were interested in the possibility of finding simple binuclear systems with linkage isomers involving a bridging cyanide group. Following our previous report on the preparation of μ-cyano-pentacyanopentaamminedicobalt(III)[8,9] we report herein the preparation and some properties of the linkage isomer μ-isocyano-pentacyanopentaamminedicobalt(III). The synthetic method employed involves the substitution of water in pentacyanoaquocobaltate(III) by the nitrogen end of cyanide in cyanopentaamminecobalt(III)

$$\mathrm{Co(NH_3)_5CN^{2+} + Co(CN)_5OH_2^{2-} \longrightarrow (NH_3)_5CoCNCo(CN)_5 + H_2O} \quad (1)$$

Experimental Section

Materials.—Cyanopentaamminecobalt(III) perchlorate was prepared and recrystallized as described by Siebert.[10] Potassium azidopentacyanocobaltate(III) was prepared by the reaction between azidopentaamminecobalt(III) chloride[11] and potassium cyanide.[12] The resins used in the ion-exchange work were Amberlite IRA 124 (hydrogen ion form) and Dowex 2X-8 (chloride ion form). All other chemicals were reagent grade.

Preparation of μ-Isocyano-pentacyanopentaamminedicobalt(III), $\mathbf{(NH_3)_5CoCNCo(CN)_5}$.—Preliminary experiments indicated that the desired reaction (eq 1) took place readily when solutions of pentacyanoaquocobaltate(III) and cyanopentaamminecobalt(III) were heated at 50°. For 0.10 *M* $Co(CN)_5OH_2^{2-}$ and 0.10 *M* $Co(NH_3)_5CN^{2+}$, the 380-nm absorption of $Co(CN)_5OH_2^{2-}$ disappeared and a new absorption at 340 nm appeared over a period of 6 hr. Guided by these observations, the following synthetic procedure was adopted. A solution 0.10 *M* in $Co(CN)_5OH_2^{2-}$ (prepared by reaction of $K_3[Co(CN)_5N_3]$ with the stoichiometric amounts of potassium nitrite and perchloric acid[13]) and 0.10 *M* in $[Co(NH_3)_5CN](ClO_4)_2$ was heated at 50° for 6 hr. After cooling in an ice–salt bath and filtering the potassium perchlorate that crystallized, the resulting solution was percolated through a cation- and an anion-exchange resin to remove any unreacted $Co(NH_3)_5CN^{2+}$ and $Co(CN)_5OH_2^{3-}$, respectively.[14] The effluent,[15] yellow in color, was concentrated at 40° in a rotary evaporator, until the solid began to separate. After cooling in an ice bath, the solid was filtered out, washed thoroughly with ice-cold water and acetone, and then air dried; yield 30%. *Anal.* Calcd for $[(NH_3)_5CoCNCo(CN)_5]\cdot H_2O$: Co, 31.3; NH_3, 22.5; C, 19.11; N, 40.85; H, 4.5. Found: Co, 30.15; NH_3, 21.9; C, 19.05; N, 40.32; H, 4.44.

Analytical Methods.—Ammonia and cobalt were analyzed as described previously.[8] Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories.

Measurements.—Visible and ultraviolet spectra were measured with a Beckman DB or a Cary 14 spectrophotometer. Infrared spectra were recorded with a Perkin-Elmer 521 spectrophotometer. Samples were potassium bromide pellets or Nujol mulls. Conductivity measurements were carried out as described before.[8]

Results and Discussion

The assignment of the structure $(NH_3)_5CoCNCo(CN)_5$ to the complex prepared in the present work is made along lines similar to those used previously for the assignment of the structure $(NH_3)_5CoNCCo(CN)_5$ to the isomeric compound.[8] The nonelectrolytic nature of the complex is established conclusively from the conductivity measurements. The specific conductance at 25° of a solution containing 1.44 g of complex/l. of solution was 1.28×10^{-5} ohm^{-1} cm^{-1}. Expressing the concentration of the complex in terms of gram-atoms of cobalt per liter of solution, the calculated molar conductance is 1.6 ohm^{-1} cm^2 mol^{-1}. The behavior of solutions of the complex toward ion-exchange resins provides additional support for the formulation of the complex as a neutral, binuclear species. The complex passes quantitatively through a cation-exchange resin but, in agreement with previous observations for the

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[1] (a) This work was supported in part by Grant GP-9669 from the National Science Foundation. (b) The convention adopted to name the compound is based on the fact that the bridging cyanide is bound to the $Co(CN)_5$ moiety through the nitrogen atom. (c) U. S. lecturer under the auspices of the Fulbright Commission, July 1969 and June 1970.

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