of the F → P nature of the 16.5-kK band[3] and inconsistent with the assignment of this band as the highest F → F transition.[4]

The present spectra are very similar to those of the $CoBrNP_3$ chromophore[12] which has a trigonal-bipyramidal geometry highly distorted toward the tetrahedron ($\alpha = 74°$) and Co-N distance which is larger than usual (2.30 Å).[13] The assignment proposed is quite similar to the present one.[12] However, by inspecting the ligand field diagrams, one expects to observe the first $A_2 \rightarrow A_2$ transition between the first two $A_2 \rightarrow E$ transitions. Possibly such a transition could be under the envelope of the ≃10-kK band which shows a ∥ component at ≃8 kK because of a displacement of the maximum in the two polarizations.

Registry No. [Co(NCS)(Me$_6$tren)] SCN·H$_2$O, 37047-98-6.

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Aminodichloroborane[1]

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Although previously studied, the chemistry of the reaction between BCl_3 and NH_3 has not been well understood.[2] Cryochemical and fast mass spectrometric inlet techniques in this laboratory have revealed that the gas-phase BCl_3-NH_3 reaction yields Cl_2BNH_2 and that the gas-phase BCl_3-H_2BNH_2 reaction yields both $ClHBNH_2$ and Cl_2BNH_2.[3] The study of these reactions was part of a continuing interest in the adaptation of cryochemical techniques to the synthesis of BN-based polymers.

Experimental Section

Commercial research grade BCl_3 and NH_3 were used without further purification. The flow system was made entirely of 10-mm o.d. copper tubing except for the 5 mm i.d. × 15 cm long Pyrex tube reactor. The reaction products had to travel about 70 cm from the point of initial reactant contact to reach the ionizing electron beam of a Bendix Model 12-107 time-of-flight mass spectrometer. The system pressure was usually maintained at about 0.5 mm as approximately indicated by thermocouple gauges. The mass spectrum of the reactor effluent was continuously displayed on an oscilloscope and recorded when desired using an X-Y recorder. The flow rates of both reactants at room temperature were adjusted and intermittently trimmed (Nupro microvalves) to produce maximum amounts of Cl_2BNH_2. When the BCl_3^+ peak disappeared, the $Cl_2BNH_2^+$ peaks were maximized, and the reaction was considered to be optimized. Continuous analyses of the reactor effluent revealed constant composition, but flow stability sufficient for appearance potential measurements could not be attained.

Infrared spectra were recorded using a Perkin-Elmer Model 221 spectrophotometer with NaCl optics and a low-temperature cell,[4] wherein the reaction products were condensed under vacuum on a cold NaCl plate. Spectra were recorded at intervals during subsequent warming to room temperature.

In the reaction and quench experiments, the products from the reactor passed through a glass trap, the temperature of which was variable to −196° as measured by a copper-constantan thermocouple. Hydrolysis experiments with aminodichloroborane were conducted by condensing the product, warming to room temperature under vacuum, and then adding excess water.

Results and Discussion

When the flow rates of the reactants, BCl_3 and NH_3, were carefully adjusted, new ion peaks, mainly in the ranges of *m/e* 35-38, 59-64, and 96-101, appeared in the mass spectrum of the reactor effluent. These ion groups were assigned in respective order to Cl^+ and HCl^+, to $ClBNH_2^+$ and its dehydrogenated ions, and to ions of the parent species. No ions heavier than *m/e* 101 ($^{37}Cl_2{}^{11}BNH_2$) were ever observed. At optimum product yield, neither reactant was observed in the reactor effluent, but this required that the molar ratio be closely controlled at $BCl_3:NH_3 = 1:2$. By passing the reactor effluent through a trap at −100°, Cl_2BNH_2 was condensed, and the remaining spectrum was solely that of HCl. Thus by observing the spectrum with the trap warm and then cold, the mass spectrum of Cl_2BNH_2 (Table I) was obtained by subtracting the contribution due to the coproduct HCl. Because of the instability of the flow system, the data of Table I were obtained by averaging a number of such observations. The absence of structure near *m/e* 65 and 95 in the product spectrum indicated that, unlike the reaction of BCl_3 with H_2BNH_2[3], the reaction with NH_3 did not form $ClHBNH_2$ and that the likely ions, Cl_2BNH^+ and Cl_2BN^+, do not appear in the spectrum of Cl_2BNH_2. To verify further that the spectrum arose only from the single compound Cl_2BNH_2, statistical isotopic calculations ($^{10}B:^{11}B = 0.244$ and $^{35}Cl:^{37}Cl = 3.087$) yielded agreement with experimental relative ion intensities to within experimental precision. The ion intensities at *m/e* 36 and 38 were decreased by increasing the flow rate of ammonia relative to that of BCl_3 further demonstrating that these peaks did not arise from Cl_2BNH_2 but rather from the parallel reaction product HCl.

A colorless and transparent annular deposit of NH_4Cl formed on the walls of the reactor at the point of mixing. A small-diameter central channel remained open allowing the gaseous reactants to continue to flow together, and the reactor appeared as a slowly extending capillary tube as the thickened walls grew downstream with continued reaction. The deposit was in a fluid state at its growing end due to the exothermicity of the reaction. Because of this heavy deposit, the reactor tube would finally close altogether, and thus the reaction period in our system was limited usually to 4-5 hr. All of these observations suggest the mechanism

$$BCl_3 + NH_3 \rightarrow Cl_2BNH_2 + HCl$$

$$HCl + NH_3 \rightarrow NH_4Cl$$

When the reaction products were passed through a trap at −45° or below, only HCl was uncondensed, while above −45°, the mass spectrum of the gases passing the trap was equivalent to that of the products sampled directly from the reactor. The product condensed at −45° or down to −196° gave no observable mass spectrum during warming to

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Table I. Low-Resolution Mass Spectrum of Cl_2BNH_2 at 70 eV

m/e	Rel intens	Ions	*m/e*	Rel intens	Ions
10	11.2	$^{10}B^+$	62	100.0	$^{37}Cl^{10}BNH^+$, $^{37}Cl^{11}BN^+$, $^{35}Cl^{11}BNH_2^+$
11	45.1	$^{11}B^+$	63	15.4	$^{37}Cl^{10}BNH_2^+$, $^{37}Cl^{11}BNH^+$
17.5	1.8	$^{35}Cl^{2+}$	64	31.7	$^{37}Cl^{11}BNH_2^+$
18.5	0.5	$^{37}Cl^{2+}$	80	1.6	$^{10}B^{35}Cl_2^+$
24	0.8	$^{10}BN^+$	81	6.7	$^{11}B^{35}Cl_2^+$
25	8.6	$^{11}BN^+$, $^{10}BNH^+$	82	1.1	$^{10}B^{35}Cl^{37}Cl^+$
26	24.3	$^{11}BNH^+$, $^{10}BNH_2^+$	83	4.1	$^{11}B^{35}Cl^{37}Cl^+$
27	18.6	$^{11}BNH_2^+$	84	0.2	$^{10}B^{37}Cl_2^+$
45	2.8	$^{10}B^{35}Cl^+$	85	0.7	$^{11}B^{37}Cl_2^+$
46	12.9	$^{11}B^{35}Cl^+$	96	8.2	$^{35}Cl_2\,^{10}BNH_2^+$
47	1.0	$^{10}B^{37}Cl^+$	97	33.2	$^{35}Cl_2\,^{11}BNH_2^+$
48	4.2	$^{11}B^{37}Cl^+$	98	6.0	$^{35}Cl^{37}Cl^{10}BNH_2^+$
59	1.2	$^{35}Cl^{10}BN^+$	99	21.0	$^{35}Cl^{37}Cl^{11}BNH_2^+$
60	9.7	$^{35}Cl^{11}BN^+$, $^{35}Cl^{10}BNH^+$	100	1.2	$^{37}Cl_2\,^{10}BNH_2^+$
61	43.8	$^{37}Cl^{10}BN^+$, $^{35}Cl^{10}BNH_2^+$, $^{35}Cl^{11}BNH^+$	101	3.3	$^{37}Cl_2\,^{11}BNH_2^+$

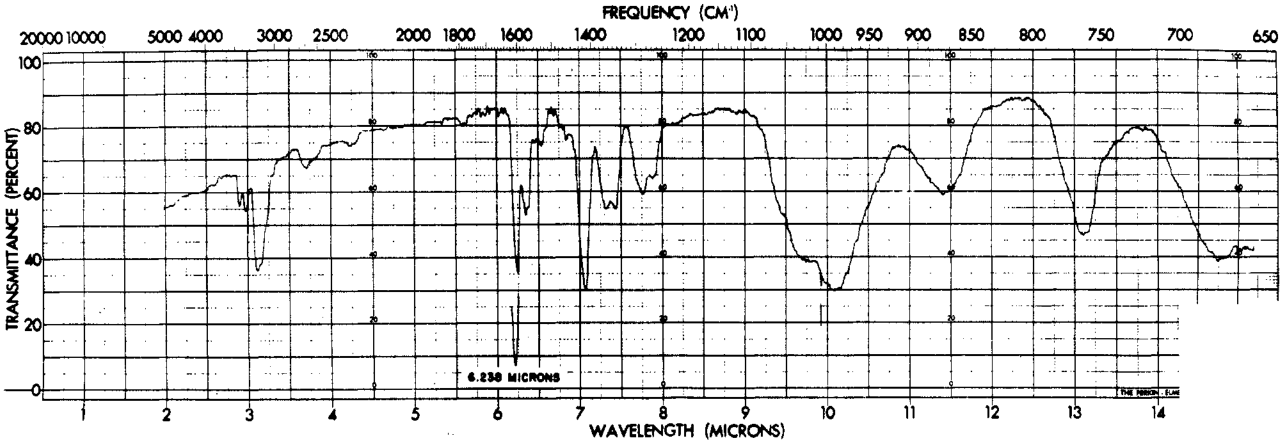

Figure 1. Infrared spectrum of condensed Cl_2BNH_2 at −196°.

room temperature. Evidently Cl_2BNH_2 reacted upon condensation to form all nonvolatile products. This colorless, transparent (almost invisible) condensate rapidly became white upon opening the trap to the atmosphere, and hence great care was exercised to exclude moisture from the system. The hydrolysis of condensed Cl_2BNH_2 with water in excess yielded HCl as the only volatile gaseous product as determined by mass spectrometric analysis. After complete evaporation of the water, a white residue of boric acid and NH_4Cl remained in accord with the equation

$$(Cl_2BNH_2)_n + 3nH_2O \rightarrow nNH_4Cl + nB(OH)_3 + nHCl$$

The infrared spectrum of condensed Cl_2BNH_2 was observed as a function of temperature, and a spectrum recorded at −196° after deposition at that temperature appears in Figure 1. With minor and smooth changes of relative intensities, the spectra were equivalent at a series of temperatures up to 25° as were those observed during warming a sample deposited at −100°. These data were completely reproducible. The only substantive change during warming was the disappearance of the band between 1330 and 1380 cm^{-1}. This band was not observed in samples deposited at −100°.

The isoelectronic equivalent of vinylidene chloride can be prepared as a reasonably stable gas, but it is immediately lost upon condensation even at −196°. If the resulting solid is a polymer, it is an uninteresting one due to its immediate reaction with H_2O.

Registry No. NH_3, 7664-41-7; BCl_3, 10294-34-5; Cl_2BNH_2, 37805-57-5.

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Ligand Action of Trifluoromethylphosphine and Bis(trifluoromethyl)phosphine toward Nickel Carbonyl and Nitrosylcobalt Carbonyl

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The displacement of one or two CO's from $Ni(CO)_4$ or one CO from $NOCo(CO)_3$ by CF_3PH_2 or $(CF_3)_2PH$ occurs quantitatively in sealed tubes in the absence of sunlight, at temperatures below 55°. The present study, taken with earlier experience,[1-3] indicates a considerable increase in bonding power when CF_3 replaces one H in phosphine and a far more moderate increase with further substitution of CF_3 for H. Moreover, there is no more than a very small increase in the

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