Figure 1. Esr spectrum of VO(dtcac)$_2$ in benzene. $\nu = 9.348$ GHz.

Table I. Esr Data for VO(S$_2$As(CH$_3$)$_2$)$_2$

Solvent	$\langle g \rangle$ (± 0.0006)	$A(^{51}\text{V})$,^{a} G	$10^{-4}A$-(^{51}V),^{b} cm^{-1}	$10^{-4}A$-(^{75}As), cm^{-1}
Benzene	1.9731	90.63	83.02	41.74
Chloroform	1.9757	90.63	81.78	41.80

^{a} Uncorrected for second-order effects. ^{b} Correct to second order.

value of the ^{75}As superhyperfine splitting constant and second-order and other effects which lead to line overlapping. Attempts to simulate the spectra[12] suggest that two equivalent arsenic nuclei giving rise to superhyperfine splitting provide the best fit to the observed data. Esr parameters are summarized in Table I. It is noted that the ^{75}As superhyperfine splitting constant for VO(dtcac)$_2$ is appreciably larger than the 26.9×10^{-4} cm^{-1} reported[13] for the ill-defined species formed from vanadium trichloride and dibutylvinylarsine. The frozen-solution spectra yielded parameters within experimental error of those reported for the analgous dithiophosphate chelates.[4] However, no ^{75}As superhyperfine splitting was observed in the frozen solutions and the spectra obtained were very similar to those obtained for other VO^{2+} complexes at low temperatures, *e.g.*, VO-(acac)$_2$.[14] This rather anomalous behavior has also been reported[15] for a frozen solution of VOF$_5{}^{3-}$ in 48% HF, which exhibits ^{19}F superhyperfine splitting when doped into (NH$_4$)$_3$AlF$_6$. Except for the possibility of a fortuitous cancelation of superhyperfine splitting in frozen solutions, the reason for the lack of superhyperfine splitting in the frozen solutions remains obscure.

The interpretation of the ^{75}As superhyperfine splitting is similar to that proposed[4] for ^{31}P superhyperfine splitting observed in vanadyl dithiophosphinates and dithiophosphates. In C_{2v} symmetry the unpaired electron resides in a ^{2}A$_1$ ground state which is approximately[16] 4.5% of d$_{z^2}$ and 94.4% of d$_{x^2-y^2}$ orbital character. The d$_{x^2-y^2}$ orbital is not strongly σ bonding with respect to sulfur but does possess the correct symmetry to interact *directly* with arsenic 4s and 4p orbitals. It is possible that the *major*

source of the ^{75}As superhyperfine splitting in VO(dtcac)$_2$ is attributable to direct vanadium 3d–arsenic 4s, 4p inter-action. However, delocalization of the unpaired electron onto the arsenic atoms *via* metal–sulfur interaction can also contribute to the observed ^{75}As superhyperfine structure. The relative importance of these two mechanisms cannot be assessed at present. The isotropic ^{75}As splitting is given by

$$A(^{75}\text{As}) = \frac{8\pi}{3} g_e g_n \beta_e \beta_n \, |\psi 4s(0)|^2 C_s^2$$

where C_s is the coefficient of the As 4s orbital in the molecular orbital containing the unpaired electron and $|\psi 4s(0)|^2$ is the 4s electron density at the nucleus. The evaluation of C_s^2 is accomplished by taking the ratio of the observed isotropic ^{75}As superhyperfine splitting, A_{obsd}, to that calculated,[17] A_{calcd}, for an unpaired electron residing totally in an arsenic 4s orbital, *i.e.*

$$C_s^2 = A_{\text{obsd}}/A_{\text{calcd}} = \frac{A_{\text{obsd}}}{3430 \text{ G}}$$

For VO(dtcac)$_2$ C_s^2 is found to be 0.0132 which is very close to the 0.0135 found for vanadyl dithiophosphates. This further illustrates the great similarity in the bonding in these VOS$_4$ chelates.

Registry No. VO(dtcac)$_2$, 37448-72-9.

(17) P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," American Elsevier, New York, N. Y., 1967, pp 20-22.

(12) Spectra were simulated using the program SIMESRQL written by Professor R. E. D. McClung. A 1000-G sweep was considered and spectra were calculated using lorentzian lines with a peak to peak width of 12 G.

(13) G. Henrici-Olive and S. Olive, *Chem. Commun.*, 596 (1969).

(14) H. A. Kuska and M. T. Rogers in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1968; D. Kivelson and S. Lee, *J. Chem. Phys.*, 41, 1896 (1964).

(15) P. T. Manoharan and M. T. Rogers, *J. Chem. Phys.*, 49, 3912 (1968).

(16) Based on a SCCC-MO calculation for VO[S$_2$P(OC$_2$H$_5$)$_2$]$_2$: H. J. Stoklosa and J. R. Wasson, unpublished results.

Single-Crystal Polarized Electronic Spectra of a CoN$_5$ Chromophore

I. Bertini, M. Ciampolini,* and D. Gatteschi

In recent years the isotropic electronic spectra of a number of trigonal-bipyramidal high-spin complexes of cobalt(II) have been measured.[1,2] Using the crystal field approach two assignments of the observed transitions were proposed.[3,4] It was felt that polarized single-crystal spectra should be useful for a substantiated assignment.
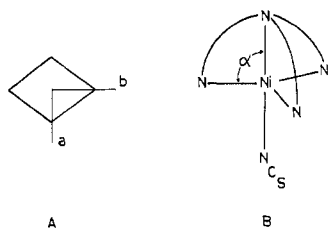
With this aim, the complex [Co(NCS)(Me$_6$tren)] SCN·H$_2$O

(1) M. Ciampolini and N. Nardi, *Inorg. Chem.*, 5, 41 (1966).

(2) M. Ciampolini, *Struct. Bonding (Berlin)*, 6, 52 (1969), and references therein.

(3) M. Ciampolini and I. Bertini, *J. Chem. Soc. A*, 2241 (1968).

(4) J. S. Wood, *Inorg. Chem.*, 7, 852 (1968).

Figure 1. (A) Crystal shape and crystallographic axes of [Co(NCS)-(Me₆tren)](SCN). (B) Schematic drawing of the [Ni(NCS)-(Me₆tren)]⁺ cation.

was prepared.[5,6] This compound is isomorphous and most probably isostructural with the nickel analog, for which a complete X-ray investigation has been carried out.[7] The single-crystal electronic spectra of this trigonal-bipyramidal CoN₅ chromophore are now reported.

Experimental Section

The complex was prepared by the general method already reported.[1] *Anal.* Calcd for $C_{14}H_{32}N_6OCoS_2$: N, 19.85; C, 39.72; H, 7.62. Found: N, 19.60; C, 39.84; H, 7.70.

Rotation and Weissenberg photographs, using Fe Kα radiation, showed that the crystals are orthorhombic, space group *Pbca*, $Z = 8$, with cell dimensions $a = 20.7$, $b = 13.9$, and $c = 15.3$ Å which compare quite well with those of the nickel analog ($a = 20.408$, $b = 13.759$, and $c = 15.002$ Å).[7] Visual examination of the X-ray photographs of the two complexes revealed no detectable differences in intensities between nickel and cobalt photographs. Therefore, it is concluded that the cobalt complex is isostructural with the nickel analog. On this basis the most highly developed face on crystals of the cobalt complex was recognized to be (001). (*Cf.* Figure 1A.)

Single-crystal electronic spectra were recorded on the (001) face along the extinction directions with the apparatus and techniques previously described.[7]

Results and Discussion

The strict isomorphism of the nickel and cobalt compounds suggests an essentially similar structure of the two complexes. The nickel chromophore has been shown to be a slightly distorted trigonal bipyramid of the type shown in Figure 1B, with N_{ax}-Ni-N_{eq} angle of $\simeq 85°$ and the N_{eq}-Ni-N_{eq} angles of 111.5, 126.0, and 120.0°.[7] Making allowance for some small changes, the cobalt chromophore may be regarded as essentially identical with the nickel one. The molecular projections along the crystallographic axes have been evaluated from the positional parameters of the latter complex.[8] On this basis the spectra recorded with the electric vector parallel to *b* should be 0.80 ∥, while those recorded with the electric vector parallel to *a* should be 0.00 ∥.

The single-crystal polarized electronic spectra, recorded along the *a* and *b* axes at 77°K, are shown in Figure 2 together with the reflectance spectrum. The room-temperature spectra differ only for a poorer resolution of the 14.8-kK band. The temperature behavior of the bands indicates that the intensity-giving mechanism is substantially an electronic one. The 16.5-kK band is ∥ polarized while the 5.8-, 14.8-, and *ca.* 21-kK bands appear to be slightly ⊥ polarized.

In a trigonal-bipyramidal chromophore three orbitally

(5) Me₆tren = N(CH₂CH₂N(CH₃)₂)₃. The crystals of the [CoXMe₆tren]X compounds (X = Cl, Br, I), which contain the C_{3v} CoN₄X chromophores, are isometric[6] and hence unsuitable for polarized spectral studies.

(6) M. Di Vaira and P. L. Orioli, *Inorg. Chem.*, 6, 490 (1967).

(7) I. Bertini, M. Ciampolini, P. Dapporto, and D. Gatteschi, *Inorg. Chem.*, 11, 2254 (1972).

(8) The atomic coordinates (x/a, y/b, z/c) of nickel and apical nitrogen: Ni, 0.1243, 0.3700; N, 0.1239, 0.5029, 0.1920. See ref 7.
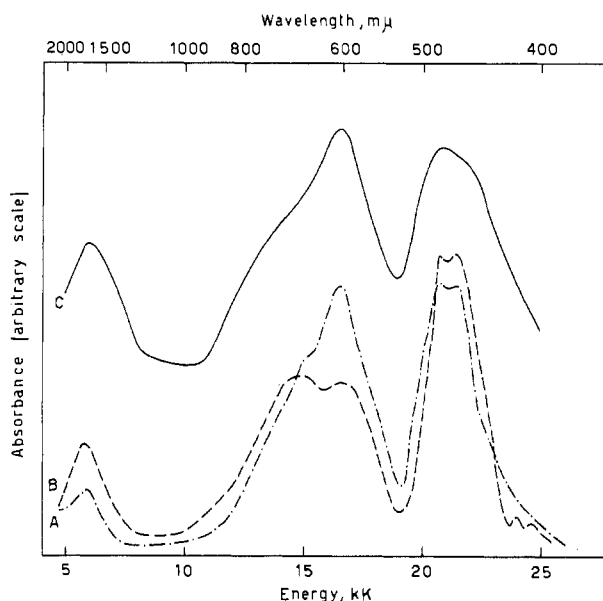
Figure 2. Single-crystal polarized electronic spectra of the [Co(NCS)-(Me₆tren)](SCN)·H₂O complex recorded with the electric vector parallel to the crystallographic *a* (A) and *b* (B) axes at 77°K and diffuse reflectance spectrum (C).

nondegenerate levels (A₂', A₁'', and A₂'' in D_{3h} formalism) are quite close to each other and the ground level depends on the radial integral ratio B_2/B_4, the $Dq(\text{ax})/Dq(\text{eq})$ ratio, and the extent of C_{3v} distortion. This situation is shown in Figure 3 where ligand field energy level diagrams are reported.

Assuming D_{3h} symmetry the expected polarizations, depending on the choice of the ground level, would be

A₂' → A₂''	no	A₂'' + A₁'' → A₂'	∥
A₁''	∥		E'	no
A₂'	no		E''	⊥
E'	⊥			
E''	no			

If C_{3v} symmetry, due to angular distortions, is assumed to be operative, the ground level is expected to be A₂ unless $Dq(\text{ax})/Dq(\text{eq}) \gg 1$. The expected polarizations both with A₂ and A₁ ground states are

A₂ → A₁	no	A₁ → A₂	no
A₂	∥	E	⊥
E	⊥		

The ∥ polarization of the 16.5 kK transition can be expected only in D_{3h} symmetry with ground levels A₁'' + A₂'' and in C_{3v} symmetry with A₂ ground level.

In C_{3v} symmetry the second highest transition, A₂ → A₂(P), is expected to be ∥ polarized as it is observed. The other three bands are expected to be ⊥ polarized. The 5.8- and 14.8-kK bands are indeed ⊥ polarized, although not in the expected 5:1 ratio. The band at $\simeq 21$ kK, assigned to the A₂ → E(P) transition, is almost unpolarized and is split into two maxima. Presumably spin–orbit effects are responsible for the splitting, since numerous levels arising from doublet terms of the free ion are expected in this region. As a matter of fact, F → P transitions of cobalt(II) complexes show a fine structure even when the complexes are quite regular.[9] Also, if deviations from C_{3v} symmetry are considered, the ⁴E level may split into as many as four

(9) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, 83, 4690 (1961); C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, 9, 397 (1955).
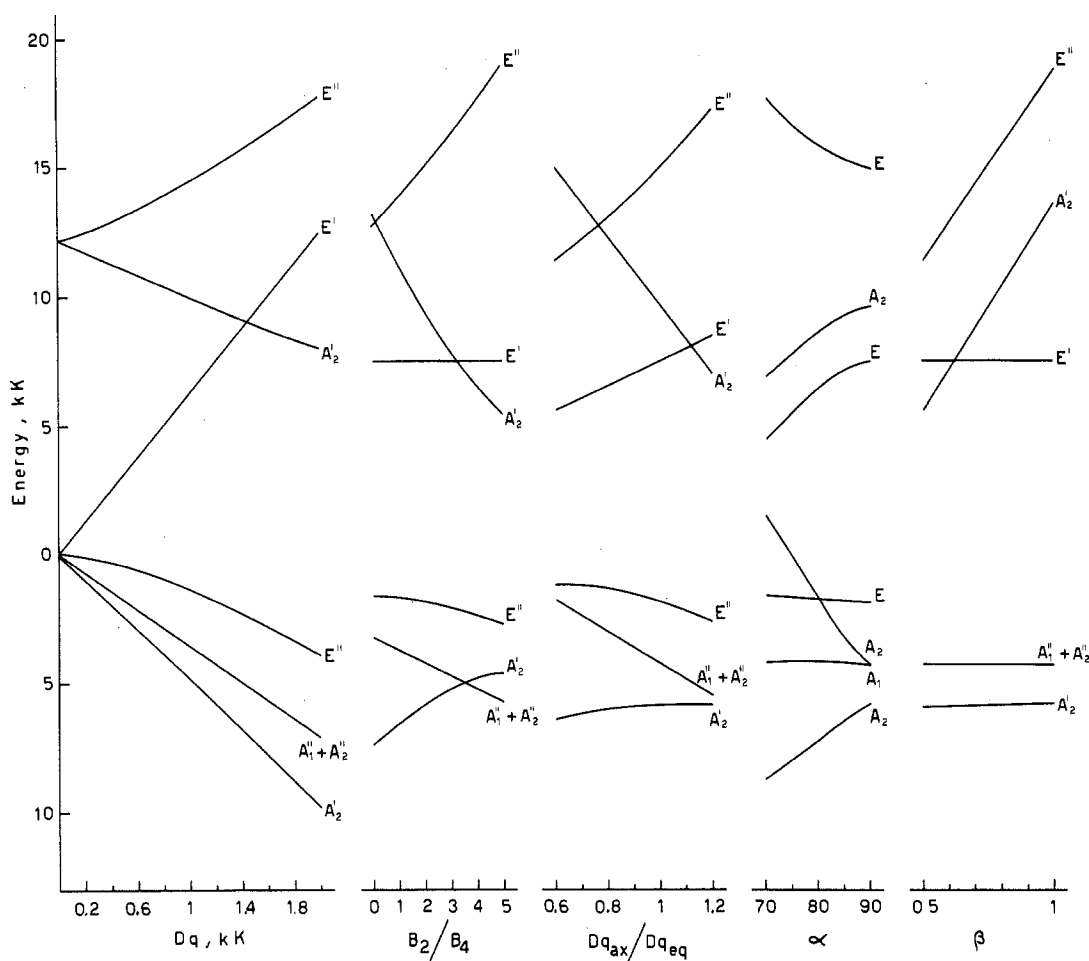
Figure 3. Energy level diagram for a cobalt(II) ion in D_{3h} trigonal-bipyramidal symmetry. $B_2/B_4 = 2.0$; $\beta = 0.75$; $Dq(ax)/Dq(eq) = 1.0$. From the left to the right the effect of changing the B_2/B_4 ratio, the $Dq(ax)/Dq(eq)$ ratio, the apical angle α, and the nephelauxetic β parameter is shown for a $Dq(eq) = 1.2$ kK. Only quartet levels are shown.

levels. A transition from the ground $^4A_2$ level to these four states may be only slightly polarized, although symmetry allowed. Distortion effects as well as spin-orbit coupling may account for the $\perp$ polarized 14.8- and 5.8-kK bands which are not as polarized as expected. In support of this interpretation, the $A_2 \rightarrow A_2(P)$ transition, which involves orbitally nondegenerate levels, is less sensitive to distortions and therefore its polarization properties are preserved.

A D_{3h} symmetry field is also capable of providing an analogous assignment. However, the A_1'' and A_2'' are ground levels only for uncommonly high B_2/B_4 ratios and for not appreciable C_{3v} distortions (for this range of B_2/B_4 ratios the order of the E' and $A_2'(P)$ levels is expected to be reversed). Moreover, the transition to the E' level, which should correspond to the 14.8-kK band, should be nonpolarized, whereas it is clearly $\perp$ polarized. For these reasons we believe that the assignment based on D_{3h} symmetry is less satisfactory than that based on C_{3v} symmetry.

It is worthwhile to recall that the polarization properties of the nickel analog have been better accounted for by D_{3h} than by C_{3v} symmetry.[7] The different symmetries probably felt by the two metal ions might be ascribed to small geometrical differences of the two chromophores. It is well known that trigonal-bipyramidal cobalt(II) complexes are commonly more distorted toward the tetrahedron than the nickel analog;[10] *i.e.*, the α angle (see Figure 1B) is <90°.

(10) L. Sacconi, *Coord. Chem. Rev.*, **8**, 351 (1972).

Table I. Observed and Calculated Spectral Band Energies for the [Co(NCS)(Me₆tren)]SCN·H₂O Complex[a]

	Frequency, kK	
Assignment	Obsd	Calcd, in C_{3v} symmetry
$^4A_2 \rightarrow {}^4A_1$	<4.0	3.0
$^4A_2$	<4.0	3.6
^4E	5.8	5.2
^4E	14.8	14.8
$^4A_2(P)$	16.5	16.9
$^4E(P)$	21.0	20.9

[a] Parameter values: $Dq(eq) = 1.2$ kK; $B_2/B_4 = 1.0$; $Dq(ax)/Dq(eq) = 1.05$; $\alpha = 85°$; $\beta = 0.70$.

Also the isostructural cubic [MBrMe₆tren]Br complexes show different α values, 84° for nickel and 81° for cobalt.[11] It also appears reasonable to assume that in the present case the cobalt complex is more C_{3v} distorted than the nickel one. The effect of such a distortion on the energy levels is principally to split the A_1'' and A_2'' levels and to increase the energy of the former level up to the crossover with the lowest E level. Reasonable fittings, *i.e.*, with the error-square sum <1 kK², have been obtained for B_2/B_4 ratios ranging 1-1.7; β, 0.65-0.75; α, 80-85°; $Dq(ax)/Dq(eq)$, 0.95-1.05; $Dq(eq)$, 1.2-1.3 kK. An indicative fitting is reported in Table I. The values of the parameters are quite reasonable and compare well with those proposed for the nickel analog. This assignment is strongly suggestive

(11) M. Di Vaira and P. L. Orioli, *Acta Crystallogr., Sect. B*, **24**, 595 (1968).

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$_2$ → A$_2$ transition between the first two A$_2$ → E transitions. Possibly such a transition could be under the envelope of the $\simeq$10-kK band which shows a ∥ component at $\simeq$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.

(12) I. Bertini, M. Ciampolini, and L. Sacconi, *J. Coord. Chem.*, 1, 73 (1971).
(13) M. Di Vaira, personal communication.

Contribution from the Chemical Engineering Department, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

Aminodichloroborane[1]

C. T. Kwon and H. A. McGee, Jr.*

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$_2$BNH$_2$ and that the gas-phase BCl$_3$–H$_2$BNH$_2$ reaction yields both ClHBNH$_2$ and Cl$_2$BNH$_2$.[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$_2$BNH$_2$. When the BCl$_3^+$ peak disappeared, the Cl$_2$BNH$_2^+$ peaks were maximized, and the reaction was considered to be optimized. Continuous analyses of the reactor effluent revealed constant com-

(1) Supported by the Air Force Office of Scientific Research through Grant AFOSR-71-2109.
(2) K. Niedenzu and J. W. Dawson, "Boron-Nitrogen Compounds," Academic Press, New York, N. Y., 1965, pp 35–36.
(3) C. T. Kwon, Ph.D. Thesis, Georgia Institute of Technology, Atlanta, Ga., 1970.

position, 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$_2$BNH$_2$ 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$_2$BNH$_2$ (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$_2$BNH$_2$,[3] the reaction with NH$_3$ did not form ClHBNH$_2$ and that the likely ions, Cl$_2$BNH$^+$ and Cl$_2$BN$^+$, do not appear in the spectrum of Cl$_2$BNH$_2$. To verify further that the spectrum arose only from the single compound Cl$_2$BNH$_2$, 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$_2$BNH$_2$ but rather from the parallel reaction product HCl.

A colorless and transparent annular deposit of NH$_4$Cl 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

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

$$HCl + NH_3 \rightarrow NH_4Cl$$
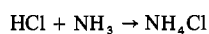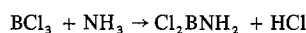
When the reaction products were passed through a trap at −45° or below, only HCl was uncondensed, while above −45°, the mass spectrum of the gases passing the trap was equivalent to that of the products sampled directly from the reactor. The product condensed at −45° or down to −196° gave no observable mass spectrum during warming to

(4) C. T. Kwon and H. A. McGee, Jr., *Inorg. Chem.*, 9, 2458 (1970).