Preparation, Spectra and X-Ray Structure of an Archetypal Coordination Compound $[BCl_3(NH_3)]$ and its Thermolysis

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Crystalline $[BCl_3(NH_3)]$ **1** is obtained in low yield from $[NH_4]Cl$ and BCl_3 in toluene, with trichloroborazine $(BClNH)_3$ **2** as the principal product; detailed NMR spectroscopic data on **1** in $CDCl_3$ are consistent with the X-ray structure, which shows intermolecular hydrogen bonding with four molecules in the unit cell [$(H\cdots Cl)_{av}$ 2.76(3) Å], B–N 1.579(4), $(B\text{–}Cl)_{av}$ 1.837(4) and $(N\text{–}H)_{av}$ 0.86(5) Å, with the boron and nitrogen environments approximately tetrahedral; thermolysis of **1** yields **2** and a TGA experiment shows that at 450 °C boron nitride is the ultimate product.

As noted by Legon and Warner,[1a] $[BF_3(NH_3)]$ was the first (*cf.* ref. 2) coordination compound of any element.[3] Its X-ray structure was determined in 1951,[4] but its identification in the gas phase was reported only in 1991,[1a] the solid readily eliminating HF to yield $BF_2(NH_2)$.[5]

Compounds of the generic type $[BX_3(NH_3)]$ were chosen by G. N. Lewis to illustrate the dative bond. However, the existence of $[BCl_3(NH_3)]$ **1** as other than a transient intermediate has hitherto been doubtful. We now report (*a*) the preparation of crystalline **1**, (*b*) detailed spectroscopic and mass spectrometric data, and (*c*) the molecular structure of **1** as established by a single crystal X-ray diffraction study.

The white, crystalline boron trichloride–ammonia adduct **1** was obtained in 6% yield by the reaction of BCl_3 with $[NH_4]Cl$ in toluene, with trichloroborazine **2** (88%) as the principal product.† Compound **1** is indefinitely stable at ambient temperature in an inert atmosphere. No attempt was made to optimise the yield of **1** at the expense of **2**. Earlier failures to prepare **1** are attributed to the fact that these invariably involved NH_3 and BCl_3 as the reactants; ammonia functioning as a base increased the tendency for **1** to undergo dehydrochlorination.

Crystalline **1** (pure on the basis of H, B, Cl and N analysis) was sparingly soluble in toluene, dichloromethane or chloroform, but appeared to decompose slowly at ambient temperature in $CHCl_3$. Suitable X-ray quality crystals were eventually obtained by recrystallisation from CH_2Cl_2 after storage at −30 °C for 5 months.‡

The IR spectrum (KBr disc) of **1** showed medium to strong bands assigned to $\nu(NH_3)$ at 3130 and 3100 cm^{-1}; $\nu(NH)$ at 1400 cm^{-1}; $\nu(BN)$ 1000 (^{10}B) and 980 (^{11}B) cm^{-1} and $\nu(BCl_3)$ at 860 (^{10}B) and 845 (^{11}B) cm^{-1}. The assignments for BX stretching modes are based partly on the relative intensities of the bands assigned to $\nu(^{10}BX)$ and $\nu(^{11}BX)$, and also on comparison with data from an argon matrix isolation IR spectroscopic study of the $NH_3\text{–}BCl_3$ system.[6]

The ^1H NMR spectrum of **1** in $CDCl_3$ at 298 K produced a broad signal which at 333 K had sharpened to a 1 : 1 : 1 triplet as the relaxation rate of ^{14}N nuclei slowed down sufficiently for coupling to be observed; this is an example of thermal decoupling. The triplet was centred at δ 2.52, ${}^1J_{^1H\text{–}^{14}N}$ 50.5 Hz. The $^{11}B\{^1H\}$ NMR spectrum showed a single sharp peak at δ 3.28 at 303 K and cooling to 198 K produced no significant change, while the ^{11}B NMR spectrum afforded a 1 : 3 : 3 : 1 quartet, ${}^2J_{^{11}B\text{–}^1H}$ 3.9 Hz. A ^{15}N NMR spectrum was obtained using the INEPT pulse sequence. This showed a −1 : −1 : 1 : 1 quartet of 1 : 1 : 1 : 1 quartets centred at δ −331.8, ${}^1J_{^{15}N\text{–}^1H}$ 70.9, ${}^1J_{^{15}N\text{–}^{11}B}$ 14.6 Hz. The ^{14}N NMR spectrum gave a single broad resonance at δ −331.8. An unsuccessful attempt was made to obtain a ^{35}Cl NMR spectrum.

The NMR spectral results demonstrate that in solution there is only one type of proton and that both N and B are coupled to three equivalent protons; and that there is only one type of boron. This rules out structures such as **1a** and **1b**, but leaves as possible candidates **1c** and **1d**.

$H[BCl_3(NH_2)]$	$[BCl_2(NH_3)_2][BCl_4]$	$[BCl_2(NH_3)]Cl$	$[BCl_3(NH_3)]$
1a	**1b**	**1c**	**1d**

The favoured solution structure of **1** is **1d** for the following reasons. First, it is consistent with the structure for the crystal, Fig. 1. Second, no ^{35}Cl NMR spectral signal was observed, suggesting that each Cl^- ligand is covalently bonded. Finally, all shifts and coupling constants are similar to those reported for $BHal_3(NR_3)$ compounds.[7] For example, ${}^1J_{BN}$ for the latter are in the range 12–19 Hz,[8] whereas compounds containing covalent BN bonds have values of 40–50 Hz. Furthermore, $\delta(^{11}B)$ for $BHal_3(NR_3)$ are in the range δ + 15 to −5, *cf.* δ +46.5 for BCl_3 or +30 for $BCl_2(NMe_2)$; and $\delta(^{15}N)$ for $BHal_3(NR_3)$ fall in the range δ −334 to −348.[7]

Crystalline **1** has four molecules of **1d** (Fig. 1) in the unit cell, with evidence for H···Cl hydrogen bonding (Fig. 2). Salient geometric parameters may be compared with selected data for some related compounds shown in Table 1.[9–11] The early X-ray structure of $[BF_3(NH_3)]$ led to the values B–N 1.60 and B–F 1.38 Å and N–B–F 107°.[4] The most recent calculated value for the B–N bond length for gaseous $[BF_3(NH_3)]$ is 1.68 ± 0.02 Å,[12] compared with the microwave spectroscopically-based value initially of 1.59 ± 0.03 Å,[1a] but revised as 1.673 Å.[1b] A calculation for $[BCl_3(NH_3)]$, using a 3-21G basis set,[13] derived values of B–N 1.611 (*cf.*[14] 1.60 Å), N–H 1.023, B–Cl 1.880 Å;

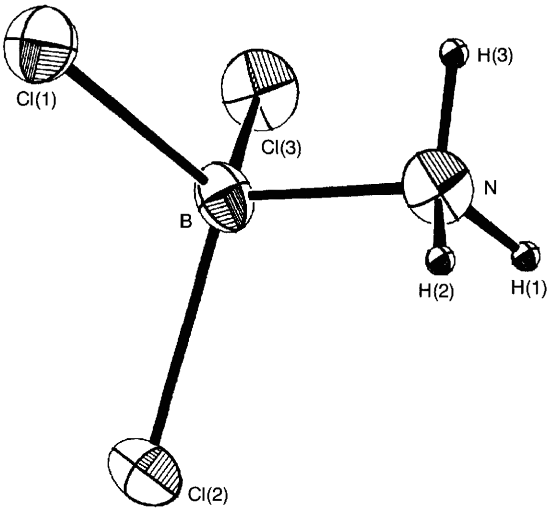


Fig. 1 The X-ray molecular structure and atom labelling scheme for $[BCl_3(NH_3)]$ **1**. Bond lengths: B–Cl(1) 1.830(4), B–Cl(2) 1.847(4), B–Cl(3) 1.834(3), B–N 1.579(4), N–H(1) 0.79(3), N–H(2) 0.88(4), N–H(3) 0.92(5) Å; bond angles: B–N–H(1) 108(2), B–N–H(2) 112(2), B–N–H(3) 104(3), H(1)–N–H(2) 103(3), H(1)–N–H(3) 123(4), H(2)–N–H(3) 106(3), Cl(1)–B–Cl(2) 111.0(2), Cl(1)–B–Cl(3) 111.5(2), Cl(2)–B–Cl(3) 111.1(2), Cl(1)–B–N 108.1(2), Cl(2)–B–N 107.6(2), Cl(3)–B–N 107.3(2)°.

Table 1 Some comparative X-ray data for BCl_3 1 : 1 adducts with nitrogen-centred donors

Compound	l(B–N)/Å	l_{av}(B–Cl)/Å	(Cl–B–N)$_{av}$/°	(Cl–B–Cl)$_{av}$/°	Ref.
$[BCl_3(NC_5H_5)]$	1.592(3)	1.837(4)	108.8(2)	110.1(3)	9
$[BCl_3(NMe_3)]$	1.575(10)	1.831(10)	109.6	109.3	10
$[BCl_3(NCMe)]$	1.562(8)	1.826(7)	106.8(4)	112.0(3)	11

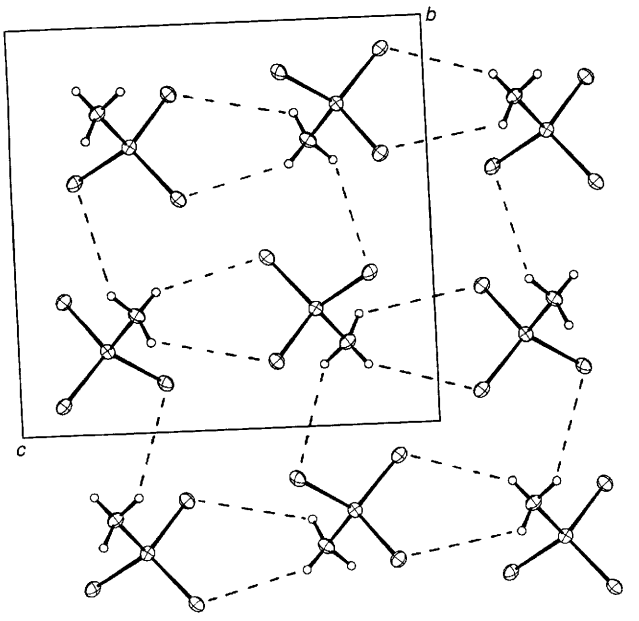
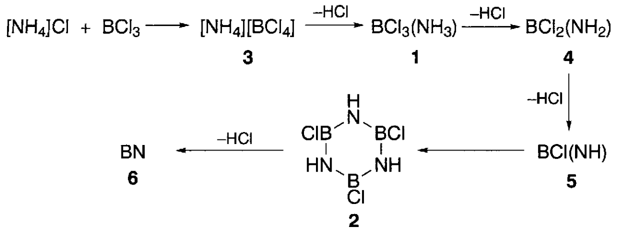


Fig. 2 The unit cell of crystalline **1**. Selected data: (H···Cl) 2.76(3) to 2.98(5), N···Cl 3.421(3) to 3.526(3) Å; N–H···Cl 120(3) to 151(4)°.



Scheme 1 Proposed reaction pathway for formation of *B,B′,B″*-trichloroborazine, and ultimately boron nitride from $[NH_4]Cl + BCl_3$

H–N–H 109.4 and Cl–B–Cl 113.2°. The lower value for the B–N bond length of 1.579(4) Å in crystalline **1** is consistent with the calculations and the notion that $BCl_3 > BF_3$ in Lewis acid strength with NH_3 as the reference base.

The likely course of the reaction leading to the borazine **2** from $[NH_4]Cl$ and BCl_3 is shown in Scheme 1. Evidence for the intermediates $[NH_4][BCl_4]$ **3**, $BCl_2(NH_2)$ **4** and BCl(NH) **5** is circumstantial. Concerning **3**, an analogous reaction from $[PyH]Cl + BCl_3$ yielded $[PyH][BCl_4]$.[15] Thermolysis of **1** in refluxing toluene afforded **2** in 68.5% isolated yield;† a thermogravimetric analysis experiment showed that **1** was completely converted to boron nitride **6** at 450 °C. The EI MS of **1** showed $[4]^+$ as the most intense ion, with evidence for further fragmentation to $[5]^+$.

The proposal that $[BCl_3(NH_3)]$ **1** might exist as a transient intermediate in the reaction between BCl_3 and NH_3 came from the matrix IR study of Hunt and Ault (*vide supra*).[6] Prior to that its existence was dubious, although the earliest data referred to materials of composition $2BCl_3{\cdot}9NH_3$ and $2BCl_3{\cdot}3NH_3$, which later were supposed to be mixture of $B(NH_2)_3$, $B_2(NH)_3$, their hydrogen chloride adducts and $[NH_4]Cl$.[16]

We thank the Leverhulme Trust for the award of an Emeritus Fellowship to M. F. L.

Received, 25th January 1995; Com. 5/00448I

Footnotes

† In a typical run, rigorously dried $[NH_4]Cl$ (154 g, 2.88 mol) and toluene (1600 cm^3) were heated under reflux (using a condenser cooled to −78 °C) while gaseous BCl_3 (380 g, 3.24 mol) was introduced during 6 h into the gaseous phase (*ca.* 3 cm above the liquid). The mixture was cooled to *ca.* 20 °C and set aside for 3 d. White crystals of $[BCl_3(NH_3)]$ **1** (24.0 g, 6%) were filtered off and dried *in vacuo*. The filtrate was evaporated to dryness *in vacuo* yielding $[BClNH]_3$ **2** (154.4 g, 88%), mp 86–86.5 °C (lit.[17] mp 83.9–85.5 °C); NMR data ([$^2H_8$]toluene): $\delta_{^1H}$ 4.5, $\delta_{^{11}B}$ 29.69, $\delta_{^{15}N}$ −276.1. Compound **2** (68.5% isolated yield) was also obtained by heating **1** (6.4 g) in toluene (100 cm^3) under reflux for 2 h.

‡ *Crystal data* for **1**: Enraf-Nonius CAD-4 diffractometer, λ(Mo-Kα) 0.71069 Å, absorption correction, full-matrix least-squares refinement with non-hydrogen atoms anisotropic, hydrogen atoms freely refined isotropic, $w = 1/\sigma^2(F)$; H_3BCl_3N, $M = 134.2$, monoclinic, $P2_1/n$, (non-standard No. 14), $a = 5.204(1)$, $b = 9.825(2)$, $c = 9.516(1)$ Å, $\beta = 92.09(1)°$, $U = 486.2$ Å^3, $F(000)$ 264; $Z = 4$, $D_c = 1.83$ g cm^{-3}, μ(Mo-Kα) = 17.1 cm^{-1}, $T = 173$ K, specimen 0.2 × 0.1 × 0.1 mm, 1240 unique reflections for $2 < \theta < 28°$, 872 reflections with $I > 2\sigma(I)$; $R = 0.033$, $R' = 0.036$, $S = 1.0$.

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