The synthesis, molecular structure and supramolecular architecture of complexes between the ammonia adduct of tris(pentafluorophenyl)boron and a series of mono and polydentate hydrogen-bond acceptors[†]

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The ammonia adduct of tris(pentafluorophenyl)boron, $(C_6F_5)_3B\cdot NH_3$, is a potentially tri-functional hydrogen-bond donor. Co-crystallisation with the bases acetonitrile, pyridine, tetrahydrofuran, tetramethylethylenediamine, 15-crown-5, 1,4-diazabicyclo[2.2.2]octane (DABCO), pyrazine and 4,4'-bipyridine results, not in donor exchange, but in the formation of supermolecules assembled through hydrogen bonding to second coordination sphere acceptors. The complexes have been characterised by elemental analysis, multinuclear NMR and single-crystal diffraction methods. The solid-state architectures range in complexity, from the hydrogen bonded pairing of $(C_6F_5)_3B\cdot NH_3$, with a single monodentate acceptor molecule (*e.g.* MeCN to form $(C_6F_5)_3B\cdot NH_3\cdot NCMe)$, through complexation with all three N–H groups to the macrocycle 15-crown-5, to the formation of infinite one-dimensional chains with pyrazine and DABCO, and to two-dimensional networks with the divergent acceptor 4,4'-bipyridine.

Introduction

Whilst tris(pentafluorophenyl)boron was first reported in 1963,¹⁻³ it has only risen to prominence since its introduction as a component of highly productive alkene polymerisation systems. In polymerisation catalysis, it is used either for alkyl abstraction (catalyst activation) or in the preparation of poorly coordinating anions.⁴ Recent studies have exploited the Lewis acidity of $(C_6F_5)_3B$ to catalyse organic transformations, including the allylstannation of aldehydes,^{5,6} ring-opening reactions of non-activated aziridines^{7,8} and the hydrosilation of unsaturated enones.⁵

The Lewis acidity of tris(pentafluorophenyl)boron is comparable to that of BF₃,⁹ and it forms robust adducts with a range of nitrogen containing Lewis bases.¹⁰ Arguably, the simplest example is the ammonia complex, which was amongst the first adducts prepared,² but until our recent investigations,¹¹ had received little attention, in sharp contrast to the aqua complex.¹²⁻¹⁶

In addition to the utilisation as a precursor to complexes of the $[(C_6F_5)_3BOH]^-$ and $[(C_6F_5)_3BO]^{2-}$ ligands, $(C_6F_5)_3B\cdot OH_2$ has been shown to form hydrogen bonded supramolecular complexes with suitable acceptors. The hydrogen atoms of the coordinated water are activated towards hydrogen bonding and readily form second coordination sphere supramolecular complexes with one¹³ or two¹⁴ further water molecules in a stepwise process that has been monitored by NMR spectroscopy.¹³ (C_6F_5)₃B·OH₂ will also form hydrogen bonds to other oxygen containing species such as MeOH, ¹BuOH,⁹ (CH₃)₂SO₂¹⁵ and 1,4-dioxane.¹⁶ The divergent nature of the 1,4-dioxane acceptor leads to the formation of an infinite one-dimensional chain.¹⁶ If a stronger base, such as an amine is employed a formal proton transfer occurs resulting in a hydrogen bonded ion pair of the form [HNRR'R'']⁺[(C₆F₅)₃BOH]^{-,7,9,17-21}

Recently, we reported that $(C_6F_5)_3B$ forms the supermolecule $(C_6F_5)_3B\cdot NH_3\cdot NH_3$ when treated with an excess of ammonia.¹¹ This suggested that $(C_6F_5)_3B\cdot NH_3$ (1) might also exhibit a rich supramolecular chemistry as a potent hydrogen-bond donor in combination with suitable basic acceptors. The ammonia adduct, with significantly less Brønsted acidity, has three potential hydrogen-bond donors leading to the possibility of two- and even three-dimensional infinite structures.

There is increasing interest in the assembly of inorganic networks without recourse to dative bonding. Very recently, the closely related cationic hydrogen-bond donor, $[Ph_3CNH_3]^+$ was shown to form supramolecular cubane and ladder fragments analogous to alkali metal phosphinimides.²² Earlier examples of intermolecular hydrogen bonding for the construction of supermolecules and infinite supramolecular architectures include the interactions between crown ethers and transition metal coordinated ammonia ligands.^{23–26} (C₆F₅)₃B·NH₃ (1) is differentiated from these examples by its combination of simplicity, neutrality and the absence of a good integral hydrogen-bond acceptor. Here, we will demonstrate that by choice of complementary hydrogenbond acceptors, infinite structures can be assembled that show parallels to metal coordination polymers.

Results and discussion

We have previously shown that the reaction between a donor-free light petroleum solution of $(C_6F_5)_3B$ and ammonia gas yields

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	B–N	B-C(11)	B-C(21)	B-C(31)	N-B-C(11)	N-B-C(21)	N-B-C(31)
1 ^{<i>a</i>11}	1.623(2)	1.627(2)	1.643(2)	1.636(2)	108.96(12)	106.17(12)	103.85(12)
	1.624(2)	1.635(2)	1.633(2)	1.639(2)	109.28(12)	103.40(12)	106.30(12)
2	1.617(2)	1.643(2)	1.639(2)	1.642(2)	107.85(9)	102.66(9)	109.38(9)
3	1.622(2)	1.640(2)	1.638(2)	1.637(2)	105.95(12)	105.35(12)	106.40(12)
4	1.608(6)	1.644(3)	1.644(3)	1.644(3)	106. 5(2)	106.5(2)	106.5(2)
5	1.599(2)	1.652 (2)	1.638(2)	1.647(2)	103.26(9)	110.28(10)	108.22(9)
6	1.601(9)	1.664(10)	1.629(10)	1.637(10)	104.9(5)	106.5(5)	108.8(5)
7	1.599(2)	1.643(2)	1.637(2)	1.652(2)	111.89(13)	103.47(12)	107.88(13)
8a	1.594(7)	1.653(8)	1.650(8)	1.640(8)	103.7(4)	108.8(4)	111.9(4)
8b	1.608(6)	1.645(6)	1.640(6)	1.637(6)	105.8(4)	109.2(4)	105.3(4)
9 ^b	1.602(3) 1.614(4)	1.641(4) 1.636(4)	1.651(3) 1.659(3)	1.639(4) 1.643(4)	110.0(2) 105.8(2)	105.4(2) 105.4(2)	105.9(2) 110.2(2)
10a	1.606(3)	1.635(3)	1.636(3)	1.633(2)	104.0(2)	106.31(14)	110.4(2)
10b	1.600(4)	1.633(4)	1.631(4)	1.648(4)	106.6(2)	107.0(2)	105.5(2)

 Table 1
 Selected bond lengths (Å) and angles (°) with standard deviations in parentheses

^{*a*} There are two independent molecules of **1** in the asymmetric unit, the atomic numbering of ref. 11 has been changed to maintain consistency with that employed herein. ^{*b*} There are two independent molecules of **9** in the asymmetric unit.

the hydrogen bonded supermolecule $(C_6F_5)_3B\cdot NH_3\cdot NH_3$ and that $(C_6F_5)_3B\cdot NH_3$ (1) can be obtained by dissolution in toluene and removal of the volatiles.¹¹ More conveniently, the same second coordination sphere ammonia adduct $(C_6F_5)_3B\cdot NH_3\cdot NH_3$ is also produced if the ether adduct $(C_6F_5)_3B\cdot OEt_2$ is employed as the $(C_6F_5)_3B$ source.

In principle, $(C_6F_5)_3B\cdot NH_3$ is a potentially tri-functional hydrogen-bond donor. The stoichiometry of the supramolecular complex formation was initially explored by the treatment of $(C_6F_5)_3B\cdot NH_3$ with either a single equivalent of a hydrogenbond acceptor or by crystallisation from a solution containing an excess of the monodentate bases acetonitrile, pyridine and tetrahydrofuran (Scheme 1).

The treatment of **1** with a modest excess of acetonitrile, followed by crystallisation from a mixed dichloromethane–light petroleum solution, yielded a sample for which the ¹H NMR and elemental analysis indicated the composition (C_6F_5)₃B·NH₃·NCCH₃ (**2**). The stoichiometry and supramolecular character of **2** was confirmed by X-ray crystallography (Fig. 1, selected geometric parameters are given in Table 1). One N-H is engaged in hydrogen bonding to an acetonitrile molecule (Fig. 1, Table 2). Both of the remaining hydrogen atoms show contacts to ortho-fluorines (Table 2). Where we observe contacts within the sum of the van der Waals radii, they are given in Table 2, however those interactions with distances approaching 2.40 Å and acute angles do not meet our interpretation of the Dunitz criteria for classification as hydrogen bonds.¹¹ The contribution of individual X-H····F-C interactions to the lattice energy will be very small but collectively their influence may be significant.¹¹ Of the two hydrogen atoms in 2 interacting with fluorine rather than nitrogen, one is engaged in a bifurcated intramolecular hydrogen bond. The other participates in a bifurcated inter/intramolecular hydrogen bond, linking two second coordination sphere adducts together in a supramolecular pair. These pairs are linked further through intermolecular offset face-to-face or edge-to-face pentafluorophenyl-pentafluorophenyl interactions to form an infinite 3D network.27 Attempts to



Scheme 1

Table 2 Hydrogen bond distances (Å) and angles (°)

	$D – H \cdots A$	<i>d</i> (D–H)/Å	$d(\mathbf{H}\cdots\mathbf{A})/\mathbf{\mathring{A}}$	$d(\mathbf{D}\cdots\mathbf{A})/\mathrm{\AA}$	∠(DHA)/°	Symmetry operation for intermolecular interaction
1 ^{<i>a</i>11}	$N(1)-H(1A)\cdots F(12)$	0.91	2.44	2.630(2)	92	
	$N(1)-H(1A)\cdots F(22)$	0.91	2.18	2.747(2)	120	
	$N(1)-H(1B) \cdots F(32)$	0.91	2.27	2.870(2)	123	
	$N(1)-H(1B)\cdots F(64^{(1)})$	0.91	2.34	3.117(2)	143	x, y - 1, z
	$N(1) - H(1C) \cdots F(12)$ N(1) - H(1C) = F(52)	0.91	2.28	2.630(2)	103	
	$N(1) - \Pi(1C) \cdots \Gamma(52)$ $N(2) - \Pi(2A) \cdots \Gamma(52)$	0.91	2.39	3.270(2) 2.954(2)	105	$r = 1, 1 \pm v, 7$
	$N(2) - H(2A) \cdots F(35^{(3)})$	0.91	2.38	2.934(2) 3.011(2)	121	x = 1, 1 + y, 2 x = 1, y, z
	$N(2)-H(2A)\cdots F(56)$	0.91	2.24	2.865(2)	125	x 1, y , z
	$N(2)-H(2B)\cdots F(42)$	0.91	2.39	2.636(2)	95	
	$N(2)-H(2B)\cdots F(43^{(4)})$	0.91	2.38	3.201(2)	151	-x, 1-v, 1-z
	$N(2) - H(2B) \cdots F(66)$	0.91	2.13	2.742(2)	124	· · ·
	$N(2)-H(2C)\cdots F(36^{(5)})$	0.91	2.31	3.160(2)	154	x - 1, y, z
_	$N(2)-H(2C)\cdots F(42)$	0.91	2.32	2.636(2)	100	
2	$N(1)-H(1A)\cdots F(12)$	0.88(2)	2.22(2)	2.7660(14)	120.5(12)	
	$N(1) - H(1A) \cdots F(36)$	0.88(2)	2.28(2)	2.6464(13)	105.1(11)	
	$N(1) - H(1B) \cdots N(4)$ N(1) - H(1C) = E(22')	0.91(2)	2.11(2) 2.24(2)	2.981(2) 2.2106(12)	158.1(13) 165.6(12)	1 2
	$N(1) - H(1C) \cdots F(22)$ $N(1) - H(1C) \cdots F(22)$	0.90(2)	2.34(2) 2.38(2)	2.2190(12) 2.9434(13)	103.0(13) 120.0(12)	1 - x, 2 - y, -2
3	N(1) - H(1C) - H(22) N(1) - H(1A) - N(51)	0.90(2) 0.93(2)	2.38(2) 2.08(2)	2.9434(13) 2.994(2)	120.9(12) 169(2)	
5	N(1) - H(1A) - F(32)	0.93(2)	2.00(2) 2.41(2)	2.794(2)	103(2) 103 7(13)	
	$N(1)-H(1B)\cdots N(41)$	0.93(2)	2.00(2)	2.926(2)	171(2)	
	$N(1)-H(1C)\cdots F(22)$	0.90(2)	2.40(2)	2.780(2)	105(2)	
4	$N(1)-H(1)\cdots O(21)$	0.88(2)	1.99(3)	2.868(3)	169(3)	
5	$N(1)-H(1A)\cdots N(46)$	0.91(2)	2.11(2)	2.906(2)	145.6(14)	
	$N(1)-H(1A)\cdots F(26)$	0.91(2)	2.33(2)	2.6714(13)	102.4(11)	
	$N(1)-H(1A)\cdots F(36)$	0.91 (2)	2.25(2)	2.7663(14)	116.1(12)	
	$N(1)-H(1B)\cdots N(43)$	0.93(2)	2.05(2)	2.893(2)	151.2(13)	1 2
($N(1)-H(1C)\cdots F(14')$	0.88(2)	2.33(2)	3.195(2)	168(2)	1 - x, 2 - y, -z
0	$N(1)-H(1A) \cdots F(12)$ N(1) H(1B) = F(22)	0.89	2.09	2.744(0)	130	
	$N(1)-H(1B) \cdots F(32)$ $N(1)-H(1B) \cdots C(1)$	0.89	2.14	2.023(0)	114	
	$N(1)-H(1C)\cdots F(22)$	0.89	2.55	2.794(7)	129	
	$N(1)-H(1C)\cdots Cl(1')$	0.89	2.58	3.295(5)	138	1 - x, 1 - y, 1 - z
7	$N(1)-H(1A)\cdots O(47)$	0.89(2)	2.11(2)	2.988(2)	169(2)	, - , ,
	$N(1)-H(1B)\cdots O(41)$	0.90(2)	2.19(2)	2.969(2)	144(2)	
	$N(1)-H(1B)\cdots F(16)$	0.90(2)	2.37(2)	2.709(2)	102(2)	
	$N(1)-H(1B)\cdots F(36)$	0.90(2)	2.25(2)	2.818(2)	121(2)	
	$N(1)-H(1C)\cdots O(50)$	0.87(2)	2.49(2)	3.102(2)	128(2)	
0	$N(1) - H(1C) \cdots O(53)$	0.87(2)	2.26(2)	3.023(2)	147(2)	
8a	$N(1) - H(1A) \cdots N(51)$ N(1) - H(1B) = E(22)	0.96(7)	2.15(7) 2.12(7)	3.035(7)	152(6)	
	$N(1) - \Pi(1B) \cdots \Gamma(22)$ $N(1) - H(1B) \cdots F(32)$	1.02(7) 1.02(7)	2.12(7) 2.39(7)	2.611(0)	96(4)	
	$N(1) - H(1B) \cdots F(25')$	1.02(7) 1.02(7)	2.39(7) 2.10(7)	3.048(6)	154(6)	1 + r v z
	$N(1) - H(1C) \cdots N(41)$	0.92(6)	2.18(6)	3 093(7)	171(5)	$1 + \lambda, y, z$
8b	$N(1)-H(1A)\cdots N(41)$	0.89(5)	2.14(5)	2.947(6)	151(4)	
	$N(1) - H(1B) \cdots N(44')$	0.82(5)	2.28(5)	3.092(6)	168(4)	x, 1/2 - y, z - 1/2
	$N(1)-H(1C)\cdots F(26)$	0.90(5)	2.25(5)	2.658(5)	107(4)	
	$N(1)-H(1C)\cdots F(32)$	0.90(5)	2.31(5)	2.728(5)	108(4)	
	$N(1)-H(1C)\cdots F(35'')$	0.90(5)	2.23(5)	2.918(5)	133(4)	x - 1, y, z
9	$N(1)-H(1A)\cdots N(78)$	0.93(3)	2.03(3)	2.936(3)	164(2)	
	$N(1) - H(1B) \cdots N(81)$	0.93(3)	1.96(3)	2.890(3)	176(2)	
	$N(1) - H(1C) \cdots F(1b)$ N(1) - H(1C) = F(22)	0.88(3)	2.30(3)	2.6/2(3) 2.742(2)	105(2) 112(2)	
	$N(1) - \Pi(1C) \cdots \Gamma(22)$ $N(2) - \Pi(2A) \cdots N(71)$	0.88(3) 0.92(3)	2.29(3) 2.03(3)	2.743(3)	112(2) 164(2)	
	$N(2)-H(2R) \cdots N(71)$ $N(2)-H(2R) \cdots N(88')$	0.92(3)	2.03(3) 2.04(3)	2.926(3)	104(2) 176(3)	$1/2 \pm r = 1/2 = r = 1/2 \pm r$
	$N(2)-H(2C)\cdots F(56)$	0.90(3)	2.04(3) 2.34(3)	2.737(3)	107(2)	1/2 + x, $1/2 - y$, $1/2 + 2$
	$N(2)-H(2C)\cdots F(66)$	0.89(3)	2.16(3)	2.689(3)	117(2)	
10a	$N(1)-H(1A)\cdots F(26)$	0.93(2)	2.36(2)	2.874(2)	114(2)	
-	$N(1)-H(1B)\cdots F(15')$	0.90(2)	2.37(2)	3.159(2)	147(2)	1 - x, 1 - y, 2 - z
	$N(1)-H(1B)\cdots F(16)$	0.90(2)	2.29(2)	2.830(2)	119(2)	
	$N(1)-H(1A)\cdots F(36)$	0.93(2)	2.30(2)	2.642(2)	101(2)	
	$N(1)-H(1C)\cdots N(41)$	0.93(2)	1.95(2)	2.872(3)	170(2)	
10b	$N(1)-H(1A)\cdots N(61)$	0.90(3)	2.18(3)	2.941(4)	142(3)	
	$N(1)-H(1B)\cdots N(41)$	0.93(4)	2.11(4)	3.001(4)	161(3)	
	$N(1)-H(1B)\cdots F(32)$ N(1) H(1C) = N(50C)	0.93(4)	2.36(3)	2.770(3)	106(2)	1/2
	$N(1) - \Pi(1C) \cdots N(50^{\circ})$	0.89(3)	2.08(3)	2.942(4)	103(3)	1/2 - x, y - 1/2, 1/2 - z

^{*a*} See footnote a in Table 1.



Fig. 1 ORTEP representation of 2 with displacement ellipsoids at 50%, hydrogen atoms not involved in hydrogen bonding have been omitted for clarity.

crystallise 1 from neat acetonitrile or acetonitrile–light petroleum mixtures, in order to obtain a sample with more than one associated acetonitrile molecule, were unsuccessful.

Compound 1 proved to be highly soluble in pyridine. Evaporation of excess pyridine under reduced pressure followed by crystallisation from a dichloromethane and light petroleum solvent mixture yielded 3. Compound 3 was found by X-ray crystallography to be the second coordination sphere complex between 1 and two pyridine molecules, (Fig. 2), and this composition was later confirmed for the bulk sample by elemental analysis and ¹H NMR spectroscopy. Attempts to prepare samples with one equivalent of pyridine, through the addition of a stoichiometric amount, or three equivalents, through crystallisation from neat pyridine, either failed to yield crystalline solids or led to the preferential formation of 3. Whilst two of the hydrogen atoms of $(C_6F_5)_3B\cdotNH_3$ form

F(24) E(35) F(34) C(26 C(34) (33) H(1C (32) H(1B N(1) F(16) F(12) C(12 C(15) F(15 N(51 C(14) =(13) C(56 C(52) F(14 C(55) C(53) (54)

Fig. 2 ORTEP representation of **3**, displacement ellipsoids are drawn at the 40% probability level, hydrogen atoms not engaged in hydrogen bonding or interactions with fluorine atoms have been omitted for clarity.

hydrogen bonds with pyridine acceptors, the third hydrogen atom is involved in an intramolecular interaction with an *ortho*-fluorine (*o*-F) atom. We note that one of the hydrogen atoms interacting with pyridine should strictly be regarded as bifurcated, with weak interactions to the *o*-F atom (Table 2).

The highly crystalline supermolecule 4 was obtained through crystallising 1 from a tetrahydrofuran and light petroleum solvent mixture. Compound 4 proved to have the composition $(C_6F_5)_3B\cdot NH_3\cdot (THF)_3$, suggesting that all three N-H groups might be participating in hydrogen bonding, a hypothesis subsequently confirmed by diffraction methods (Fig. 3). In the solid state, 4 has perfect three-fold symmetry, crystallising in space group $R\overline{3}$ with the three-fold axis running along the B–N bond.²⁸ The three symmetry-related hydrogen bonds show a $H \cdots O$ separation of 1.99(3) Å with a N–H \cdots O angle of 169(3)°. Since each of the N-H groups is exclusively engaged in intermolecular hydrogen bonding, this is a rare example of an amine adduct of $(C_6F_5)_3B$ that is not supported by intramolecular N-H···F-C hydrogen bonds.¹¹ The absence of an intramolecular hydrogen bond does not have a significant influence on the B-N bond length in 4, which is similar to the other structures reported herein. The second coordination sphere complexes of 4 pack together to form a two-dimensional net through offset face-to-face $C_6F_5 \cdots C_6F_5$ interactions leaving hexagonal voids in which highly disordered solvent molecules are situated. The $R\bar{3}$ space group is found for a number of structures with an EPh₃ fragment indicating similar features in the supramolecular lattices.²⁹ It is possible that the observed preference for the crystallisation of a species with three hydrogen bonded THF molecules is directed by the favourable nature of the resulting crystal lattice, which optimises the $C_6F_5 \cdots C_6F_5$ interactions.



Fig. 3 ORTEP representation of **4** with displacement ellipsoids at the 40% probability level and viewed almost along the three-fold rotation axis. The THF molecules show disorder, with alternative sites for the methylene group of C(24); atom numbers with suffixes ' and " are related by the symmetry operations 1 - y, x - y, z and 1 - x + y, 1 - x, z, respectively.

The current study is predominantly concerned with the nature of the crystalline supermolecules resulting from the interaction of

Table 3 $\,^{1}{\rm H}$ and $^{19}{\rm F}$ NMR data recorded in CDCl₃ (unless otherwise stated) for the NH₃ group and the fluorine atoms

	ortho-F/ppm	<i>meta</i> -F/ppm	para-F/ppm	¹ H NH ₃ /ppm
$1 (C_6 D_6)^{11}$	-135.3	-162.9	-155.5	2.67
1	-135.0	-161.9	-154.6	4.75
2	-135.4	-162.8	-155.8	4.81
$3(C_6D_6)$	-134.9	-163.4	-156.5	4.93
$4(C_6D_6)$	-135.2	-162.9	-155.6	3.14
5	-135.3	-163.0	-156.2	5.48
6	-134.4	-163.0	-156.4	5.46
$7(C_6D_6)$	-134.1	-164.7	-158.5	5.39
8b	-135.4	-162.3	-155.1	4.80
9	-135.4	-162.5	-155.3	5.03
10b	-135.3	-162.7	-155.8	5.45

1 with basic hydrogen-bond acceptors. Amongst the monodentate bases, only in the THF example did we find interactions with more than two hydrogen bonded acceptor molecules in the solid state. However, we cannot rule out the possibility that tris complexes are formed in solution in the presence of excess base. Indeed one might expect tris complexation to be favoured for the more basic nitrogen donors, despite the fact that we did not obtain any crystalline examples.

During the course of the routine spectroscopic characterisation, it was readily apparent that determining the nature of any second coordination sphere interactions maintained in solution would present a significant challenge (selected spectroscopic data are provided in Table 3). The hydrogen bonds are obviously highly labile and the spectra are therefore averaged. Evidently, the ¹⁹F NMR data, which are diagnostic for the formation of $(C_6F_5)_3B$ adducts, show little value for identifying the second sphere coordination.

The ¹H chemical shift of the NH₃ group is unsurprisingly more sensitive to the hydrogen bonding environment. In comparing the data in Table 3, it is worth noting that reference compound 1 itself is not hydrogen bond free and that it exhibits relatively weak intramolecular N-H···F interactions, (Table 2). Furthermore, there is a significant ¹H NMR chemical shift difference between 1 in d_6 -benzene and d_1 -chloroform solutions, which we attribute to the mode of solvation. While it is apparent that second sphere coordination complexes are present in solution, we can say little about their precise composition. However, the distinctly highfield value for compound 4 does appear significant. Despite the fact that the solid-state structure has three hydrogen bonds, the solution-phase NMR data are much closer to those of 1 than the supermolecule formed with 15-crown-5, (7), which is discussed below. It therefore seems probable that the second coordination sphere complex, with the weak monodentate tetrahydrofuran acceptors, is largely dissociated in the benzene solution.

The isolation of **3** and **4** demonstrated that supermolecule formation through hydrogen bonding to two or three N–H groups was possible. We therefore reasoned that second coordination sphere complexes formed through multiple hydrogen bonds to 'chelating' bases would be both accessible and, where sterically compatible, exhibit increased stability.

The treatment of **1** with one equivalent of tetramethylethylenediamine (TMEDA) was expected to yield a compound with the composition (C_6F_5)₃B·NH₃·(TMEDA) (**5**) (Scheme 2). The reaction was conducted in dichloromethane solution and



the crude product subsequently recrystallised from toluene, yielding X-ray quality crystals. Confounding expectations, the structural solution revealed, not **5**, but $(C_6F_5)_3B\cdot NH_3$, $[(CH_3)_2NCH_2CH_2N(CH_3)_2CH_2Cl]^+$ and Cl^- entities, comprising compound **6**. It appears that $(C_6F_5)_3B\cdot NH_3$ serves to promote nucleophilic attack of the amine upon the dichloromethane solvent, giving rise to the observed cation, since the reaction does not otherwise take place under ambient conditions. Similar reactivity has been observed in the presence of electrophilic metal centres.³⁰⁻³² We have subsequently found that NEt₃ will also react with CH₂Cl₂ in the presence of **1**.³³ The solution-phase stability of $(C_6F_5)_3B\cdot NH_3$ and the instability of tertiary amine adducts¹¹ suggest that it is indeed **1**, and not $(C_6F_5)_3B$, that is the electrophile responsible but this mechanism awaits further investigation.

The solid state structure of **6** consists of the ion pair $[(CH_3)_2NCH_2CH_2N(CH_3)_2(CH_2CI)][CI]$ co-crystallised with compound **1**. The cation is unremarkable and resembles previously characterised $[NR_3(CH_2CI)]^+$ salts.³⁴ Within the context of this study, two molecules of **1** and two Cl⁻ ions (Fig. 4) can be regarded as forming a hydrogen bonded supramolecular complex. The N–H bonds involved in hydrogen bonding to the Cl⁻ ion are both strictly bifurcated since each also interacts with an *o*-F. The remaining N–H group participates in a single short hydrogen bond to a third *o*-F. Cation–anion interactions are restricted to a close contact between a hydrogen atom from a methyl group of the quaternary ammonium and the chloride ion.



Fig. 4 ORTEP representation of **6** indicating the hydrogen bonding interaction of $(C_6F_5)_3B$ ·NH₃ and Cl⁻ anion pairs and the relative positions of the associated counter cations. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms not engaged in hydrogen bonding have been omitted for clarity.

In light of the reactivity towards dichloromethane, X-ray quality crystals of **5** were grown from a toluene solution. TMEDA chelates to two of the ammonium hydrogen atoms of $(C_6F_5)_3B\cdot NH_3$. One of these H-atoms is also engaged in a trifurcated arrangement with two *o*-F atoms. The third hydrogen is hydrogen bonded to the *para*-fluorine (*p*-F) of a symmetry-related $(C_6F_5)_3B\cdot NH_3$ molecule so that the solid-state architecture is composed of supramolecular dimers (Fig. 5). These dimers are linked further through aryl–perfluoraryl interactions with a toluene solvent molecule disordered about a centre of symmetry to generate infinite 1D chains.



Fig. 5 ORTEP representation of 5 illustrating the formation of pairs of $(C_6F_5)_3B\cdot NH_3$ molecules through hydrogen bonding, the disordered toluene solvent molecule and the hydrogen atoms on the TMEDA have been omitted for clarity and displacement ellipsoids are at the 40% probability level.

Since TMEDA forms a 1 : 1 supramolecular complex with 1, and compound 4 demonstrates the ability to hydrogen bond through all three N–H donors, we reasoned that a suitable macrocyclic acceptor might engage all the protic hydrogens. A literature survey revealed an extensive chemistry of second coordination sphere complexes between crown ethers and ammonia adducts of both transition metals and main group Lewis acids.^{22–25} The success of the Stoddart and Colquhoun group in crystallographically characterising 1 : 1 complexes between F₃B·NH₃ and H₃B·NH₃ with 18-crown-6 is of obvious relevance.³⁵ Attempts to prepare a supermolecule suitable for crystallographic investigation by treating 1 with 18-crown-6, dibenzo-18-crown-6 and 12-crown-4 were unsuccessful. However, 1 and 15-crown-5 co-crystallised from dichloromethane solution to give 7 (Scheme 3). Multinuclear



Scheme 3

NMR spectra and elemental analysis were consistent with the 1 : 1 second coordination sphere adduct formulation $(C_6F_5)_3B\cdot NH_3\cdot 15$ crown-5 and this was confirmed by diffraction methods.

As is the case for F₃B·NH₃·18-crown-6,³⁵ all three of the ammonia hydrogen atoms on 1 are hydrogen bonded to 15crown-5 (Fig. 6 and Table 2). However, while the macrocycle of $F_3B \cdot NH_3 \cdot 18$ -crown-6 retained pseudo D_{3d} symmetry and a nearsymmetrical triangle of hydrogen bonds, with a short average H...O distance very similar to that in 4 at 1.99 Å,³⁵ the arrangement in 7 is somewhat more complex and the hydrogen bonds somewhat longer. The first of the hydrogen atoms is involved in a single hydrogen bond to an oxygen atom $H(1A) \cdots O(47)$ 2.11(2) Å. The second is engaged in a trifurcated hydrogen bond to one of the 15-crown-5 oxygen atoms $H(1B) \cdots O(41) 2.19(2)$ Å and to two *o*-F atoms of the C_6F_5 rings. The third hydrogen atom participates in a bifurcated hydrogen bonding to two oxygen atoms of the 15-crown-5, while one of the hydrogen bonds is of medium length (2.26(2) Å) the other is long (2.49(2) Å). The molecules pack together through offset face-to-face and edgeto-face $C_6F_5 \cdots C_6F_5$ interactions. In 7, accommodating all three N-H in hydrogen bonds to the 15-crown-5 macrocycle requires considerable distortion from the near ideal geometries observed for $F_3B \cdot NH_3 \cdot 18$ -crown-6 and 4, and the poor crystallinity of the 18-crown-6 analogue is difficult to rationalise.



Fig. 6 ORTEP representation of **7** illustrating the hydrogen bonding of $(C_6F_5)_3$ B·NH₃ to 15-crown-5, displacement ellipsoids are drawn at the 40% probability level with the hydrogen atoms not engaged in hydrogen bonding and the solvent molecule have been omitted for clarity.

The successful structural characterisation of discrete supermolecules, assembled through hydrogen bonding to convergent acceptors, suggested that choice of a divergent acceptor would lead to the generation of infinite supramolecular assemblies related to those formed between di- or tri-functional Lewis acids and divergent bases.

The treatment of **1** with an excess of pyrazine in dichloromethane solution and subsequent crystallisation yielded a sample



Scheme 4

with the gross composition $1 \cdot NC_4 H_4 N$ by elemental analysis and ¹H NMR (Scheme 4). However, X-ray diffraction revealed that although the sample appeared homogeneous there were two crystal forms present. The first crystal characterised proved to be a minor component with the composition $\{(C_6F_5)_3B\cdot NH_3\}_2$ {pyrazine}₃, (**8a**, Fig. 7). Each molecule of $(C_6F_5)_3B\cdot NH_3$ is hydrogen bonded to two pyrazine acceptors. One pyrazine bridges two symmetry-related molecules of $(C_6F_5)_3B\cdot NH_3$ with a crystallographic inversion centre at the centroid of the pyrazine ring. The second pyrazine is terminal: N(44) does not accept a hydrogen bond. The remaining N–H group is engaged in an intramolecular hydrogen bonding interaction to two *o*-F atoms in a very similar fashion to that present in **3**. There is a further N–H… F contact to a *meta*-

 $\begin{array}{c} H(1B^{*}) \\ F(25) \\ F(26) \\ F(2$

Fig. 7 ORTEP representation of the structure of **8a** with displacement ellipsoids at 50% and hydrogen atoms on the pyrazine molecules being omitted for clarity.

fluorine (m-F) of a neighbouring molecule. One of the two pyrazine molecules is involved in a somewhat displaced aryl-perfluoroaryl interaction.

The second crystal selected reflected the elemental analysis result and thus the bulk composition $(C_6F_5)_3B\cdot NH_3$ pyrazine, **8b**, and was therefore assumed to be the major component (Fig. 8). The supramolecular structure consists of infinite 1D 'zig-zag' chains constructed from hydrogen bonds between two ammonia hydrogen atoms, each to a pyrazine acceptor (Fig. 9). The third N-H participates in a trifurcated hydrogen bond



Fig. 8 Molecular ORTEP representation of **8b** illustrating the hydrogen bonding within the asymmetric unit, displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms not engaged in hydrogen bonding and the dichloromethane solvent molecule have been omitted for clarity.



Fig. 9 An illustration of the infinite chains of **8b**, solvent molecules and intramolecular hydrogen bonds have been omitted for clarity.

to two intramolecular *o*-F atoms and one intermolecular *m*-F atom, linking the chains together to form a 2D sheet. These sheets are linked further through offset face-to-face $C_6F_5 \cdots C_6F_5$ interactions, extending the network into a third dimension.

The reaction between 1,4-diazabicyclo[2.2.2]octane (DABCO) and 1 proceeds similarly to that with pyrazine, giving crystals with a 1 : 1 composition confirmed by ¹H NMR, elemental analysis and X-ray crystallography (9, Fig. 10). Two of the ammonia hydrogen atoms in each molecule are involved in intermolecular hydrogen bonding to the DABCO molecules, thus forming a 1D chain. The third is engaged in a bifurcated hydrogen bond to two ortho-fluorine atoms. In contrast to 8b however, rather than 'zigzagging' the chain follows more of a wave-like pattern, with half the DABCO molecules lying disordered over two positions between two rows of $(C_6F_5)_3B\cdot NH_3$ in the crystal structure (Fig. 11). The other DABCO molecules lie along two parallel lines defining the peaks and troughs of the wave-like chain. The infinite hydrogen bonded chains observed for 8b and 9 resemble 1D coordination polymers in which pyrazine,³⁶⁻³⁹ DABCO⁴⁰⁻⁴² or 4,4'-bipyridine⁴³⁻⁴⁵ bridge transition metals through dative interactions. As was the case for **8b**, the infinite chains of **9** pack together through offset face-to-face C₆F₅ interactions.



Fig. 10 ORTEP representation of 9 illustrating the asymmetric unit, the hydrogen bonding within the structure and the disorder of one of the DABCO molecules, displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms not involved in hydrogen bonding and the dichloromethane solvent molecules have been omitted for clarity.



Fig. 11 Illustrating the one-dimensional chains of 9, only the major components of the disordered DABCO molecules are shown here and the dichloromethane solvent molecules have been omitted for clarity.

The nature of the supramolecular complex formed between 1 and 4,4'-bipyridine (bipy) proved to be dependent upon, but not to directly follow, the molar ratio employed. The treatment of 1 with one equivalent of bipy yielded a crystalline material (10a). X-Ray analysis showed that the 4,4'-bipyridine molecule is hydrogen bonded to two $(C_6F_5)_3B\cdot NH_3$ (Fig. 12). There is an inversion centre on the C(44)–C(44') bond at the centre of the bipy ligand, hence the asymmetric unit contains one $(C_6F_5)_3B\cdot NH_3$ molecule and half a bipy molecule. Since only one N-H is engaged in an intermolecular hydrogen bond, the structure can therefore be regarded as related to 2. As was found for 2, one of the remaining hydrogen atoms participates in a bifurcated intramolecular hydrogen bond to two ortho-fluorine atoms, whilst the other is involved in a bifurcated hydrogen bond to one intra and one intermolecular fluorine atom (Table 2). However, unlike 2, the intermolecular hydrogen bonds are divergent and generate one-dimensional chains through the $N-H \cdots F$ contacts.



Fig. 12 ORTEP representation of 10a showing a molecule of $(C_6F_5)_3B\cdot NH_3$ hydrogen bonded to each end of the 4,4'-bipyridine molecule. Displacement ellipsoids are drawn at the 50% probability level.

Spectroscopic characterisation of the material obtained at a 1:1 molar ratio of 1 and bipy, in contrast to the structurally characterised crystals of 10a, indicated that 1 and bipy were present in a 2:3 molar ratio (10b). However, X-ray quality crystals with this composition were only obtained from solutions in which bipy was in excess. The solid-state structure of 10b was determined

by X-ray crystallography (Fig. 13). Each ammonia hydrogen is involved in hydrogen bonding to a bipy molecule, which links in turn to another $(C_6F_5)_3B\cdot NH_3$ molecule. This connectivity extends infinitely, generating a two-dimensional hydrogen bonded grid (Fig. 14). The grids are linked together through displaced aryl-perfluoroaryl interactions between one C_6F_5 ring and half of a bipyridine and through face-to-face and vertex-to-face $C_6F_5 \cdots C_6F_5$ interactions. Diagonal threads can be traced through the grid shown in Fig. 14, which closely resemble the 'zig-zag' chains present in **8b**.



Fig. 13 ORTEP representation of **10b** showing a molecule of $(C_6F_5)_3B\cdot NH_3$ forming hydrogen bonds to three 4,4'-bipyridine molecules. Hydrogen atoms not involved in hydrogen bonding and the disordered dichloromethane molecule have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.



Fig. 14 The extended ring system generated in 10b, the solvent and the C_6F_5 rings have been omitted for clarity.

The 'chicken-wire' grid pattern of **10b** (Fig. 14), is a familiar motif in hydrogen bonded organic networks,⁴⁶⁻⁴⁷ while twodimensional coordination polymers are often found in a squaregrid arrangement.⁴⁸⁻⁵⁰ To the best of our knowledge, this example is unique amongst the metal-free networks, in that the grid is not interpenetrated. The absence of interpenetration is a consequence of the steric bulk of the $(C_6F_5)_3B$ group and small size of the NH₃ node.

The ammonia adduct of tris(pentafluorophenyl)borane forms discrete second coordination sphere complexes with monodentate and convergent polydentate hydrogen-bond acceptors in solution and in the solid-state. The solution structures are labile and the resulting crystals do not always reflect the composition of the solution medium from which they are grown. Indeed, even in the presence of a large excess of base, discrete complexes in which all three N-H groups participate in intermolecular hydrogen bonding were only obtained in the cases of 4 and 7. Where the N-H groups are not engaged in intermolecular hydrogen bonding, they participate in intramolecular interactions with ortho-fluorines very similar to those we observed for amine adducts of $(C_6F_5)_3B$. such that the intramolecular hydrogen bonding in 2 resembles $(C_6F_5)_3B\cdot N(R)H_2$ and 3 resembles that in $(C_6F_5)_3B\cdot N(R)_2H^{11}$ Interactions between pentafluorophenyl groups play a significant role in directing the supramolecular architectures of these lattices. Particularly noteworthy is the $R\bar{3}$ space group found for 4, which suggests that its favourable supramolecular architecture can play a part in dictating the composition of the crystalline second coordination sphere adduct.

The careful control of stoichiometry and the addition of divergent acceptors results in the transition from supermolecules incorporating a single molecule of 1 to more complex structures, such as 8a and 10a and on to infinite one-dimensional chains 8b and 9 and the infinite two-dimensional grid 10b. In this respect, it is possible to draw close structural analogies to the field of supramolecular coordination chemistry despite the much weaker character of these hydrogen bonding interactions.

Experimental

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques in pre-dried glassware. Solvents were dried using an appropriate drying agent and distilled under nitrogen prior to use, dichloromethane (CaH₂), light petroleum (Na–K alloy), tetrahydrofuran (sodium– benzophenone) and toluene (sodium). Samples for NMR analysis were prepared using degassed deuterated solvents dried over activated 4 Å molecular sieves. NMR spectra were obtained using a Bruker Avance DPX300 spectrometer at 23 °C, *J* values are given in Hz. Elemental analyses were carried out at the London Metropolitan University. Pyridine and acetonitrile were dried over activated 4 Å molecular sieves and all other reagents were used as supplied from commercial sources.

$(C_6F_5)_3B \cdot NH_3$ (1)

Following a modification of the literature procedure,¹¹ (C_6F_5)_3B·NH_3 was prepared directly from the ether adduct of tris(pentafluorophenyl)boron. Gaseous ammonia was passed over a solution of B(C_6F_5)_3·OEt₂ (5.94 g, 10.1 mmol) in light petroleum (*ca.* 350 cm³) for 5 min, during which time a white precipitate of (C_6F_5)_3B·NH_3·NH_3 formed. The precipitate was filtered, dried under vacuum and the resulting solid was dissolved in toluene (40 cm³). The second equivalent of ammonia was removed with the toluene under vacuum, yielding crude **1**. Colourless crystals of (C_6F_5)_3B·NH_3 were obtained through crystallisation

from a dichloromethane and light petroleum solvent mixture at -25 °C. The NMR data were in agreement with the literature data.¹¹

(C₆F₅)₃B·NH₃·CH₃CN (2)

Acetonitrile (0.3 cm³, 5.7 mmol) was added to a solution of $(C_6F_5)_3B$ ·NH₃ (0.529 g, 1 mmol) in dichloromethane (5 cm³) at room temperature. X-Ray quality colourless crystals were grown upon the addition of light petroleum (5 cm³) and cooling the solution to -25 °C. Elemental analysis found: C 41.6, H 0.8, N 4.8. Calculated for $C_{20}H_6BF_{15}N_2$: C 42.1, H 1.0, N 4.9. $\delta_{\rm H}$ /ppm (300.1 MHz, CDCl₃) 4.81 (3H, s, NH₃), 1.97 (3H, s, CH₃). $\delta_{\rm C}$ /ppm (75.5 MHz, {¹H}, CDCl₃) 116.90 (CN), 2.15 (CH₃). $\delta_{\rm B}$ /ppm (96.3 MHz, CDCl₃) -9.38. $\delta_{\rm F}$ /ppm (282.4 MHz, CDCl₃) -135.4 (6F, m, *o*-F), -155.8 (3F, t, ³ $J_{\rm FF}$ 20, *p*-F), -162.8 (6F, m, *m*-F).

$(C_6F_5)_3B\cdot NH_3\cdot (C_5H_5N)_2$ (3)

(C₆F₅)₃B·NH₃ (0.64 g, 1.2 mmol) was dissolved in pyridine (1 cm³) at room temperature giving a colourless solution. The removal of the solvent under vacuum afforded a fine powdery material with the composition (C₆F₅)₃B·NH₃·(C₅H₅N)₂ (0.72 g, 1.2 mmol, 99%). X-Ray quality crystals were obtained by recrystallisation from a dichloromethane–light petroleum solution. Elemental analysis found: C 48.8, H 1.9, N 6.15. Calculated for C₂₈H₁₃BF₁₅N₃: C 48.9, H 1.9, N 6.1. $\delta_{\rm H}$ /ppm (300.1 MHz, C₆D₆) 8.24 (6H, m, C₅H₅N), 6.91 (2H, m, C₅H₅N), 6.58 (6H, m, C₅H₅N), 4.93 (3H, br, NH₃). $\delta_{\rm B}$ /ppm (96.3 MHz, C₆D₆) –10.2. $\delta_{\rm F}$ /ppm (282.4 MHz, C₆D₆) –134.9 (6F, m, *o*-F), –156.5 (3F, t, ³J_{FF} 20, *p*-F) –163.4 (6F, m, *m*-F).

$(C_6F_5)_3B\cdot NH_3\cdot (C_4H_8O)_3$ (4)

(C₆F₅)₃B·NH₃ (0.44 g, 0.83 mmol) was dissolved in THF (3 cm³). The solution was cooled slowly to -25 °C to afford colourless crystals. The solvent of crystallisation was removed under reduced pressure. Elemental analysis found: C 48.3, H 3.5, N 2.0. Calculated for C₃₀H₂₇BF₁₅NO₃: C 48.35, H 3.65, N 1.9. $\delta_{\rm H}$ /ppm (300.1 MHz, C₆D₆) 3.52 (6H, m, C₄H₈O), 3.14 (3H, br, NH₃), 1.45 (6H, m, C₄H₈O). $\delta_{\rm C}$ /ppm (75.5 MHz, {¹H}, C₆D₆) 67.86 (CH₂), 25.84 (CH₂). $\delta_{\rm B}$ /ppm (96.3 MHz, C₆D₆), -9.98. $\delta_{\rm F}$ /ppm (282.4 MHz, C₆D₆), -135.2 (6F, m, *o*-F), -155.6 (3F, t, ³J_{FF} 21, *p*-F), -162.9 (6F, m, *m*-F).

$(C_6F_5)_3B\cdot NH_3\cdot (CH_3)_2NCH_2CH_2N(CH_3)_2\cdot C_7H_8$ (5)

Tetramethylethylenediamine (0.2 cm³, 1.3 mmol) was added to a solution of (C₆F₅)₃B·NH₃ (0.529 g, 1 mmol) in toluene (5 cm³) and the resulting reaction mixture was then cooled to -25 °C affording colourless X-ray quality crystals. The solvent of crystallisation was removed under reduced pressure. Elemental analysis found: C 44.6, H 2.8, N 6.2. Calculated for C₂₄H₁₉BF₁₅N₃: C 44.9, H 3.0, N 6.5. δ_{H} /ppm (300.1 MHz, CDCl₃) 5.48 (3H, s, NH₃), 2.29 (4H, s, CH₂), 2.10 (12H, s, CH₃). δ_{C} /ppm (75.5 MHz, {¹H}, CDCl₃) 57.7 (CH₂), 45.74 (CH₃). δ_{B} /ppm (96.3 MHz, CDCl₃) –9.97. δ_{F} /ppm (282.4 MHz, CDCl₃) –135.3 (6F, m, *o*-F), –156.2 (3F, t, ³J_{FF} 21, *p*-F), –163.0 (6F, m, *m*-F).

$(C_6F_5)_3B\cdot NH_3\cdot |(CH_3)_2NCH_2CH_2N(CH_3)_2CH_2C||C|$ (6)

Tetramethylelthylenediamine (TMEDA) (0.2 cm³, 1.3 mmol) was added to a solution of $(C_6F_5)_3B\cdot NH_3$ (0.529 g, 1 mmol) in CH₂Cl₂ (4 cm³). The solution was layered with light petroleum and cooled slowly to -25 °C to afford colourless crystals, which were unsuitable for X-ray crystallography. The crystals were separated by filtration and recrystallised from toluene–light petroleum to afford colourless X-ray quality crystals. δ_H /ppm (300.1 MHz, CDCl₃) 5.66 (2H, s, CH₂Cl), 5.46 (3H, br, NH₃), 3.81 (2H, t, ³J_{HH} 6.0, CH₂), 3.42 (6H, s, CH₃), 2.72 (2H, t, ³J_{HH} 6.0, CH₂), 2.26 (6H, s, CH₃). δ_C /ppm (75.5 MHz, {¹H}, CDCl₃) 69.65 (CH₂Cl), 58.86 (CH₂) 54.13 (CH₂), 49.74 (CH₃), 45.11 (CH₃). δ_B /ppm (96.3 MHz, CDCl₃) -10.10. δ_F /ppm (282.4 MHz, CDCl₃) -134.4 (6F, m, *o*-F), -156.4 (3F, t, ³J_{FF} 20, *p*-F) -163.0 (6F, m, *m*-F).

$(C_6F_5)_3B \cdot NH_3 \cdot (C_{10}H_{20}O_5)$ (7)

A solution of (C₆F₅)₃B·NH₃ (0.45 g, 0.9 mmol) in toluene (5 cm³) was treated with 15-crown-5 (0.17 cm³, 0.9 mmol) at ambient temperature affording a colourless emulsion. The solvent was removed under reduced pressure giving a solid, which when washed with light petroleum gave an elemental analysis consistent with the composition (C₆F₅)₃B·NH₃·15-crown-5 (0.60 g, 0.8 mmol, 93%). Recrystallisation from dichloromethane–light petroleum yielded X-ray quality crystals of **7**. Elemental analysis found: C 44.8, H 3.1, N 1.8. Calculated for C₂₈H₂₃BF₁₅NO₅: C 44.9, H 3.1, N 1.9. $\delta_{\rm H}$ /ppm (300.1 MHz, CDCl₃) 5.39 (3H, br, NH₃), 3.46 (20H, s, 15-crown-5). $\delta_{\rm B}$ /ppm (96.3 MHz, CDCl₃) –10.7. $\delta_{\rm F}$ /ppm (282.4 MHz, CDCl₃) –134.1 (6F, d, ³J_{FF} 20, *o*-F), –158.5 (3F, t, ³J_{FF} 20, *p*-F), –164.7 (6F, t, ³J_{FF} 20, *m*-F).

$\{ (C_6F_5)_3B\cdot NH_3 \}_2 \{ \mu - C_4H_4N_2 \}_3 \text{ (8a) and } \\ [\{ (C_6F_5)_3B\cdot NH_3 \} \{ \mu - C_4H_4N_2 \}]_{\it n} \text{ (8b) }$

A solution of $(C_6F_5)_3B\cdot NH_3$ (0.529 g, 1 mmol) in dichloromethane (3 cm³) at room temperature was treated with a dichloromethane solution (3 cm³) of pyrazine (0.080 g, 1 mmol). The reaction mixture was then cooled to -25 °C overnight to yield two visually indistinguishable sets of X-ray quality crystals **8a** (towards the top of the Schlenk tube) and the major constituent, **8b**. The solvent of crystallisation was removed under reduced pressure. Elemental analysis (for **8b**) found: C 43.3, H 1.0, N 6.8. Calculated for C₂₂H₇BF₁₅N₃: C 43.4, H 1.2, N 6.9. δ_H /ppm (300.1 MHz, CDCl₃) 4.80 (3H, s, NH₃), 8.57 (4H, s, CH). δ_C /ppm (75.5 MHz, {¹H}, CDCl₃) 145.56 (CH). δ_B /ppm (96.3 MHz, CDCl₃) –9.08. δ_F /ppm (282.4 MHz, CDCl₃) –135.4 (6F, m, *o*-F), –155.1 (3F, m, *p*-F), –162.3 (6F, m, *m*-F).

$[{(C_6F_5)_3B\cdot NH_3}{\mu-N(CH_2CH_2)_3N}]_n$ (9)

The addition of 1,4-diazabicyclo-[2.2.2]-octane (DABCO) (0.168 g, 1.5 mmol) in CH₂Cl₂ (5 cm³) to a solution of (C₆F₅)₃B·NH₃ (0.529 g, 1 mmol) in CH₂Cl₂ (5 cm³) resulted in the immediate precipitation of a fine white precipitate. X-Ray quality crystals were grown by layering dilute solutions of (C₆F₅)₃B·NH₃ in CH₂Cl₂ and DABCO in light petroleum and cooling to -25 °C. Elemental analysis found: C 45.1, H 2.0, N 6.4. Calculated for C₂₄H₁₅BF₁₅N₃: C 45.0, H 2.4, N 6.55. $\delta_{\rm H}$ /ppm (300.1 MHz, CDCl₃) 5.03 (3H, s, NH₃), 2.76 (12H, s, CH₂). $\delta_{\rm C}$ /ppm (75.5 MHz, {¹H}, CDCl₃) 47.20

 Table 4
 Crystallographic data

	2	3	4	5	9	7	8a	8b	6	10a	10b
Chemical formula	(C ₆ F ₅) ₃ BNH ₂ CH ₃ CN	, (C ₆ F ₅) ₃ BNH ₃ . 2(C ₅ H ₅ N)	(C ₆ F ₃) ₃ BNH ₃ . 3C ₄ H ₈ O	(C ₆ F ₅) ₃ BNH ₃ . (CH ₃) ₂ NCH ₂ - CH ₂ N-(CH ₃) ₂ . 1/2(C ₇ H ₈)	$(C_6F_5)_3BNH_3$. $(CH_3)_2NCH_2$. $CH_2N-(CH_3)_2$. $CH_3CI^+ \cdot CI^-$	$(C_6F_5)_3BNH_3$. $C_{10}H_{20}O_5$. $1/2CH_2CI_2$	2(C ₆ F ₅) ₃ BNH ₃ . 3(C ₄ H ₄ N ₂)	(C ₆ F ₅) ₃ BNH ₃ . C ₄ H ₄ N ₂ . CH ₂ Cl ₂	$(C_6F_5)_3BNH_3, C_6H_{12}N_2, CH_2CI_2$	2(C ₆ F ₅), BNH ₃ . C ₁₀ H ₈ N ₂	$2((C_6F_5)_3BNH_3)$. $3(C_{10}H_8N_2)$. CH_2CI_2
$M_{ m r}/{ m g}~{ m mol}^{-1}$	570.1	687.22	801.2	691.3	730.2	791.8	1298.3	694.0	726.1	1214.2	1611.6
Crystal system	Triclinic	Monoclinic	Trigonal	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\overline{1}$	$P2_1/c$	$R\overline{3}$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\overline{1}$	C2/c
a/Å	9.2789(7)	9.9845(14)	15.1659(11)	10.1180(10)	10.6506(3)	10.5169(8)	7.8554(5)	7.7724(9)	17.9464(3)	10.5017(18)	20.5853(16)
$b/ m \AA$	9.9867(6)	25.873(2)	15.1659(11)	10.5752(9)	12.6740(5)	12.1454(6)	36.146(3)	29.639(3)	16.8703(4)	11.412(5)	16.0102(10)
$c/\text{\AA}$	11.7257(10)	10.7558(11)	26.9397(3)	16.231(3)	13.1477(9)	12.4667(7)	9.0775(4)	11.8275(7)	19.6562(3)	11.547(3)	22.0129(11)
$\alpha/^{\circ}$	101.070(7)	90	90	72.134(6)	111.1075(9)	84.845(4)	90	90	90	96.404(5)	06
$\beta/^{\circ}$	100.590(7)	105.237(9)	90	87.620(2)	106.7322(4)	83.918(4)	105.391(5)	110.192(8)	106.4170(11)	111.114(19)	114.527(7)
y/°	103.133(6)	90	120	62.421(9)	104.885(3)	82.348(5)	90	90	90	115.928(10)	06
V/\AA^3	1008.64(13)	2680.8(5)	5366.1(6)	1454.7(3)	1450.72(12)	1564.7(2)	2485.1(3)	2557.2(4)	5708.5(2)	1099.7(6)	5600.3(7)
T/K	140(1)	120(2)	140(1)	140(1)	140(1)	120(2)	140(1)	140(1)	120(2)	140(1)	140(1)
Z	7	4	9	2	2	2	2	4	8	1	4
Reflections measured	15631	28 347	17 637	22 902	12150	33 117	36470	25 421	63 159	15 562	27 979
Unique reflections, R_{ii}	^μ 5727, 0.024	6054, 0.033	1878, 0.100	8244, 0.029	3774, 0.051	7162, 0.036	5698, 0.074	3336, 0.092	$10\ 021,\ 0.075$	5007, 0.073	4295, 0.037
Observed data	4290	4817	1530	6031	2558	5273	4957	2289	8069	3689	3353
wR_2, R_1 (observed dat	a) 0.083, 0.032	0.083, 0.037	0.127, 0.057	0.100, 0.039	0.186, 0.063	0.086, 0.039	0.220, 0.127	0.098, 0.049	0.102, 0.048	0.094, 0.043	0.094, 0.043
wR_2, R_1 (all data)	0.087, 0.049	0.090, 0.052	0.138, 0.075	0.107, 0.061	0.205, 0.097	0.097, 0.063	0.226, 0.143	0.111, 0.093	0.112, 0.083	0.103, 0.068	0.101, 0.063
Largest difference pea	k 0.29	0.27	0.32	0.49	1.41	0.29	0.47	0.34	0.27	0.31	0.29

(CH₂). δ_B /ppm (96.3 MHz, CDCl₃) –9.35. δ_F /ppm (282.4 MHz, CDCl₃) –135.4 (6F, m, *o*-F) –155.3 (3F, m, *p*-F) –162.5 (6F, m, *m*-F).

$\begin{array}{l} \{(C_6F_5)_3B{\cdot}NH_3\}_2\{\mu{-}C_{10}H_8N_2\}\ (10a)\ and\\ [\{(C_6F_5)_3B{\cdot}NH_3\}_2\{\mu{-}C_{10}H_8N_2\}_3]_{\prime\prime}\ (10b) \end{array}$

A solution of 4,4'-bipyridine (0.156 g, 1 mmol) in CH₂Cl₂ (4 cm³) was added to a solution of (C₆F₅)₃B·NH₃ (0.529 g, 1 mmol) in CH₂Cl₂ (4 cm³). The solution was cooled slowly to -25 °C to yield X-ray quality crystals of **10a** and a crystalline solid (**10b**). Spectroscopic data for **10b**: $\delta_{\rm H}$ /ppm (300.1 MHz, CDCl₃) 8.61 (6H, dd, *J* 4.6 and 1.5, CH), 7.51 (6H, dd, *J* 4.5 and 1.6, CH), 5.45 (3H, br, NH₃). $\delta_{\rm C}$ /ppm (75.5 MHz, {¹H}, CDCl₃) 150.7 (CH), 146.1 (C), 122.0 (CH). $\delta_{\rm B}$ /ppm (96.3 MHz, CDCl₃) –9.43. $\delta_{\rm F}$ /ppm (282.4 MHz, CDCl₃) –135.3 (6F, m, *o*-F) –155.8 (3F, t, ³*J*_{FF} 20, *p*-F), –162.7 (6F, m, *m*-F). Due to the presence of a mixture of **10a** and **10b**, satisfactory elemental analysis could not be obtained.

Preparation of X-ray quality crystals of ${(C_6F_5)_3B\cdot NH_3}_2{\mu-C_{10}H_8N_2}_3$ (10b)

A solution of $(C_6F_5)_3B\cdot NH_3$ (0.529 g, 1 mmol), in CH_2Cl_2 (4 cm³) was added to a solution of 4,4'-bipyridine (0.468 g, 3 mmol) in CH_2Cl_2 . The solution was then cooled to -25 °C to afford colourless crystals of **10b**.

X-Ray crystallography

Diffraction data for **3**, **7** and **9** were collected by the EPSRC Crystallography Service at the University of Southampton on a Bruker-Nonius KappaCCD diffractometer and the data were processed using the DENZO/SCALEPACK programs.⁵¹ All other data were collected at UEA on an Oxford Diffraction Xcalibur-3 CCD diffractometer, and processed using the CrysAlis-CCD and RED programs. In each case, the structure was determined by direct method routines in the SHELXS program and refined by full-matrix least-squares methods on F^2 in SHELXL⁵² within the WinGX program suite.⁵³ The results are collated in Table 4. Scattering factors for neutral atoms were taken from literature values.⁵⁴

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