Crystal and Supramolecular Structures of Complexes* of BF_3NH_3 and BH_3NH_3 with 18-Crown-6

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The macrocyclic polyether 18-crown-6 ($C_{12}H_{24}O_6$) readily forms crystalline 1 : 1 complexes with the adducts BF_3NH_3 and BH_3NH_3. Crystals of the solvates $BF_3NH_3{\cdot}C_{12}H_{24}O_6{\cdot}CH_2Cl_2$ and $BH_3NH_3{\cdot}C_{12}H_{24}O_6{\cdot}MeOH$ were suitable for *X*-ray crystallographic investigation. In both cases, the crystal structures reveal that 18-crown-6 adopts an all-*gauche* conformation with pseudo D_{3d} symmetry in which the intermolecular N–H $\cdots$ O hydrogen-bonding interactions between the macrocyclic polyether and the adducts are associated directly with the triangle of oxygen atoms on the complexing face of the crown.

Crystalline complexes of 18-crown-6 ($C_{12}H_{24}O_6$) with ammonium ($[NH_4]Br{\cdot}C_{12}H_{24}O_6{\cdot}2H_2O$)[1] and substituted ammonium {$[NH_3(CH_2Ph)]SCN{\cdot}C_{12}H_{24}O_6$,[2] $[NH_3(CH_2COPh)]PF_6{\cdot}C_{12}H_{24}O_6$,[3] $[NH_3Me]ClO_4{\cdot}C_{12}H_{24}O_6$,[4] $[NH_3(NH_2)]ClO_4{\cdot}C_{12}H_{24}O_6$,[4] and $[NH_3(OH)]ClO_4{\cdot}C_{12}H_{24}O_6{\cdot}0.5H_2O$}[4] ions have been reported and their crystal structures determined. To date, all have been found to have 1 : 1 stoicheiometry and to involve hydrogen bonding[5] of the ammonium centre to oxygen atoms on the crown ether ring, which invariably adopts an all-*gauche* conformation with pseudo D_{3d} symmetry. Although the detailed nature of the hydrogen bonding differs[4] from complex to complex, the structure of the complex is necessarily of a face-to-face type.

18-Crown-6 also forms[6] crystalline adducts with transition-metal ammines. In the case of *trans*-$[PtCl_2(PMe_3)(NH_3)]$, where a 2 : 1 crystalline adduct is formed[7] between the *neutral* transition-metal ammine and 18-crown-6, all six of the oxygen atoms are hydrogen bonded in approximately trigonal fashions, the two NH_3 ligands approaching from opposite faces of the crown. This change in adduct stoicheiometry is, however, not accompanied by any modification in the symmetry of the macrocycle. Transition-metal complexes both neutral,[7] *e.g.* *trans*-$[PtCl_2(NH_3)_2]$, and charged,[8] *e.g.* $[Cu(NH_3)_4(H_2O)]^{2+}$, which carry at least two *trans*-related NH_3 ligands, form crystalline hydrogen-bonded polymers with 1 : 1 stoicheiometry in which the complex and the crown ether alternate along the polymer axis.

In view of the above observations, it seemed highly likely that *neutral* complexes formed between ammonia and certain main-group compounds (*e.g.* electron-deficient BX_3 compounds) would also bind through hydrogen bonding with crown ethers. Here, we report on the preparation and structural characterisation of complexes formed between (*i*) BF_3NH_3 and 18-crown-6 and (*ii*) BH_3NH_3 and 18-crown-6.

Experimental

Materials and Methods.—18-Crown-6 was obtained from Hopkin and Williams and BH_3NH_3 from Ventron GMBH. BF_3NH_3 was prepared by passing NH_3 over a stirred solution of $BF_3{\cdot}OEt_2$ in CCl_4 until there was no further evolution of fumes. The white solid was recrystallised from water. Infrared spectra were recorded on a Perkin-Elmer 157 G grating spectrophotometer. Microanalyses were carried out by the Characterisation and Measurement Group of I.C.I. Mond Division. Melting points were determined in air using a hot-stage microscope and are uncorrected.

Preparation of $BF_3NH_3{\cdot}C_{12}H_{24}O_6$.—$BF_3NH_3$ (137 mg, 1.62 mmol) was dissolved in warm water (5 cm^3). The solution was filtered, cooled to room temperature, and added to a filtered solution of 18-crown-6 (428 mg, 1.62 mmol) in water (10 cm^3). Within 30 s, precipitation was evident. The mixture was allowed to stand at room temperature overnight, after which the white crystalline solid was filtered off, washed with water, and dried *in vacuo*. Yield 336 mg (59%), m.p. 160—162 °C (Found: C, 41.3; H, 7.75; N, 4.15. Calc. for $C_{12}H_{27}BF_3NO_6$: C, 41.3; H, 7.80; N, 4.00%). The i.r. spectrum (Nujol mull) of the 1 : 1 complex contained the following characteristic bands: 3 250, 3 198, and 3 155 (NH), and 1 110 cm^{-1} (CO). The NH bands are shifted considerably to lower frequency compared with those [3 348, 3 283, and 3 160 cm^{-1}] present[9] in BF_3NH_3 itself. A small portion (20 mg) of $BF_3NH_3{\cdot}C_{12}H_{24}O_6$ was dissolved in CH_2Cl_2 (1 cm^3), and pentane (5 cm^3) was layered on top of the solution. After 2 d, the mixture contained crystals of the complex solvated with CH_2Cl_2. They proved to be suitable for examination by *X*-ray crystallography. Crystals with similar morphologies were also obtained from CH_2Cl_2–heptane and CH_2Cl_2–OEt_2 solvent mixtures.

Preparation of $BH_3NH_3{\cdot}C_{12}H_{24}O_6$.—A solution of BH_3NH_3 (41 mg, 1.34 mmol) in MeOH (5 cm^3) was filtered and added to a solution of 18-crown-6 (354 mg, 1.34 mmol) in MeOH (10 cm^3) which also had been filtered. Although the onset of formation of fine needles occurred almost instantaneously, the mixture was set aside at room temperature overnight. The white crystalline solid was then filtered off, washed with MeOH, and dried *in vacuo*. Yield 190 mg (47%), m.p. 147—149 °C (Found: C, 48.8; H, 10.5; N, 5.00. Calc. for $C_{12}H_{30}$-

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* Amminetrifluoroboron–1,4,7,10,13,16-hexaoxacyclo-octadecane–dichloromethane (1/1/1) and amminetrihydroboron–1,4,7,10,13,16-hexaoxacyclo-octadecane–methanol (1/1/1), respectively.

Supplementary data available (No. SUP 23753, 20 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

BNO_6: C, 48.8; H, 10.2; N, 4.75%). The i.r. spectrum (Nujol mull) of the 1 : 1 complex contained the following characteristic bands: 3 314, 3 280, 3 252, and 3 208 (NH), 2 333, 2 295, 2 258, and 2 215 (BH), and 1 110 cm^{-1} (CO). The assignments to B–H stretching frequencies are based upon an interpretation [10] of the i.r. spectrum of $BH_3(NHMe_2)$ which refers to characteristic absorptions for B–H stretching in the co-ordinated BH_3 in the region 2 260—2 400 cm^{-1}. Recrystallisation of the complex from MeOH afforded crystals solvated with MeOH and suitable for *X*-ray structural investigation.

Crystal Structure Determinations.—*Crystal data for* $BF_3NH_3{\cdot}C_{12}H_{24}O_6{\cdot}CH_2Cl_2$. $M = 434$, Orthorhombic, $a = 8.351(2)$, $b = 14.715(4)$, $c = 17.143(3)$ Å, $U = 2\,107$ Å^3, space group $P2_12_12_1$, $Z = 4$, $D_c = 1.37$ g cm^{-3}, and μ(Cu-K_α) = 36 cm^{-1}. Data for a small single crystal (approximate dimensions, 0.2 × 0.2 × 0.3 mm) were measured using monochromatized Cu-K_α radiation ($\lambda = 1.541\ 78$ Å, graphite monochromator) on a Nicolet R3m diffractometer. A total of 1 647 independent reflections were measured ($\theta \leqslant 58°$) using the ω-scan measuring routine and, of these, 1 476 had $|F_o| > 3\sigma(|F_o|)$ and were considered to be observed. The data were corrected for absorption using an empirical method and based upon 288 ψ measurements. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically. All three NH_3 hydrogens were clearly resolved in a difference electron-density map and the group refined as a rigid body. The other hydrogens were placed at calculated positions and allowed to ride on their parent carbons. Refinement was by block-cascade full-matrix least squares to $R = 0.048$. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system.

Crystal data for $BH_3NH_3{\cdot}C_{12}H_{24}O_6{\cdot}CH_3OH$. $M = 327$, Orthorhombic, $a = 8.416(3)$, $b = 13.685(7)$, $c = 16.923(8)$ Å, $U = 1\,949$ Å^3, space group $P2_1cn$, $Z = 4$, and $D_c = 1.12$ g cm^{-3}. Since the crystals are highly unstable * and decompose instantly on removal from solution, a small single crystal (approximate crystal dimensions 0.3 × 0.3 × 0.4 mm) was transferred *under solution* into a Lindemann glass capillary tube, excess of solution was carefully drawn off, and the tube was sealed leaving a small drop surrounding the crystal. Data collection conditions were the same as those described above for $BF_3NH_3{\cdot}C_{12}H_{24}O_6{\cdot}CH_2Cl_2$. In view of the unstable nature of the crystals and the probability of radiation damage, data were collected using a fast scan speed (29.3° min^{-1}) for all reflections. A total of 1 086 independent reflections were measured ($\theta \leqslant 50°$) and, of these, 689 had $|F_o| > 3\sigma(|F_o|)$ and were considered to be observed. Total *X*-ray exposure time was about 4 h during which the counting rate for the check reflections fell by approximately 10%. The structure was solved by direct methods. In view of the shortage of observed data, only the O, N, and B atoms were refined anisotropically. The carbon atoms were refined isotropically. The bis(methylene) hydrogen atoms were placed at calculated positions and allowed to ride on their parent carbon atoms. The MeOH molecule was disordered. Neither the NH_3 nor the BH_3 hydrogen atoms were sufficiently resolved to permit refinement. Refinement was by block-cascade full-matrix least squares to $R = 0.107$. As before, computations were carried out on an Eclipse S140 computer using the SHELXTL program system.

Table 1. Atomic co-ordinates (× 10^4) for $BF_3NH_3{\cdot}C_{12}H_{24}O_6{\cdot}CH_2Cl_2$

Atom	*x*	*y*	*z*
O(1)	2 707(4)	1 195(2)	6 866(2)
C(2)	1 111(5)	1 471(3)	6 975(4)
C(3)	1 049(7)	2 341(3)	7 410(3)
O(4)	1 622(4)	3 052(2)	6 932(2)
C(5)	1 622(6)	3 896(3)	7 326(3)
C(6)	2 280(6)	4 611(3)	6 803(3)
O(7)	3 931(4)	4 422(2)	6 683(2)
C(8)	4 730(6)	5 086(3)	6 217(3)
C(9)	6 449(6)	4 853(3)	6 174(3)
O(10)	6 641(4)	4 041(2)	5 742(2)
C(11)	8 255(5)	3 759(3)	5 706(3)
C(12)	8 391(6)	2 886(3)	5 257(3)
O(13)	7 682(4)	2 179(2)	5 706(2)
C(14)	7 791(6)	1 321(3)	5 332(3)
C(15)	7 043(6)	623(3)	5 852(3)
O(16)	5 388(4)	779(2)	5 919(2)
C(17)	4 605(6)	133(3)	6 383(3)
C(18)	2 850(6)	379(3)	6 449(3)
C(19)	−1 205(10)	2 448(5)	9 662(5)
Cl(1)	−89(3)	3 423(1)	9 474(1)
Cl(2)	−121(3)	1 468(1)	9 513(1)
N	5 235(4)	2 592(2)	6 880(2)
H^a	6 092	2 524	6 512
H^b	4 768	3 185	6 824
H^c	4 434	2 138	6 784
B	6 138(7)	2 602(4)	7 702(3)
F(1)	7 173(4)	3 332(2)	7 715(2)
F(2)	6 994(4)	1 810(2)	7 762(2)
F(3)	5 012(4)	2 667(2)	8 280(2)

Table 2. Atomic co-ordinates (× 10^4) for $BH_3NH_3{\cdot}C_{12}H_{24}O_6{\cdot}MeOH$

Atom	*x*	*y*	*z*
O(1)	3 285	−953(8)	4 842(7)
C(2)	3 231(31)	−1 017(14)	5 658(11)
C(3)	2 616(30)	−1 899(15)	5 850(13)
O(4)	961(21)	−1 964(10)	5 714(7)
C(5)	79(27)	−2 812(15)	5 881(12)
C(6)	−1 599(30)	−2 726(18)	5 689(13)
O(7)	−1 845(21)	−2 593(11)	4 870(8)
C(8)	−3 486(30)	−2 459(17)	4 636(12)
C(9)	−3 519(34)	−2 437(18)	3 794(13)
O(10)	−2 864(18)	−1 510(8)	3 507(6)
C(11)	−2 921(33)	−1 434(14)	2 657(11)
C(12)	−2 106(29)	−479(15)	2 428(13)
O(13)	−489(20)	−577(10)	2 618(7)
C(14)	457(30)	285(16)	2 397(13)
C(15)	2 119(33)	116(16)	2 605(12)
O(16)	2 180(23)	169(8)	3 457(8)
C(17)	3 766(33)	3(17)	3 696(11)
C(18)	3 944(31)	−37(15)	4 567(10)
N	868(25)	−1 959(10)	3 831(8)
B	1 519(38)	−2 886(21)	3 350(16)
O(19)	−883(51)	60(24)	9 502(16)
C(20)	622(69)	37(29)	9 231(24)

Results and Discussion

Tables 1 and 2 present the atomic co-ordinates, Tables 3 and 4, the bond lengths, and Tables 5 and 6, the bond angles for $BF_3NH_3{\cdot}C_{12}H_{24}O_6{\cdot}CH_2Cl_2$ and $BH_3NH_3{\cdot}C_{12}H_{24}O_6{\cdot}MeOH$, respectively. Other selected geometrical parameters are summarized for these respective complexes in Figures 1 and 2 as well as in their captions. In view of the formal positive charge which can be associated with the nitrogen atom in both BF_3NH_3 and BH_3NH_3, the ability of these *neutral* addition

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* On one occasion, a few crystals in MeOH in a stoppered vial on a laboratory bench exploded spontaneously some time after they had been in contact with a nickel spatula.

Table 3. Bond lengths (Å) for $BF_3NH_3{\cdot}C_{12}H_{24}O_6{\cdot}CH_2Cl_2$

O(1)-C(2)	1.406(6)	O(1)-C(18)	1.402(5)
C(2)-C(3)	1.482(7)	C(3)-O(4)	1.412(6)
O(4)-C(5)	1.415(5)	C(5)-C(6)	1.486(6)
C(6)-O(7)	1.421(6)	O(7)-C(8)	1.427(5)
C(8)-C(9)	1.478(7)	C(9)-O(10)	1.415(5)
O(10)-C(11)	1.412(5)	C(11)-C(12)	1.502(6)
C(12)-O(13)	1.422(5)	O(13)-C(14)	1.420(5)
C(14)-C(15)	1.496(6)	C(15)-O(16)	1.406(6)
O(16)-C(17)	1.400(5)	C(17)-C(18)	1.514(7)
C(19)-Cl(1)	1.741(8)	C(19)-Cl(2)	1.722(8)
N-H^a	0.960	N-H^b	0.960
N-H^c	0.960	N-B	1.599(7)
B-F(1)	1.379(6)	B-F(2)	1.370(6)
B-F(3)	1.369(7)		

Table 4. Bond lengths (Å) for $BH_3NH_3{\cdot}C_{12}H_{24}O_6{\cdot}MeOH$

O(1)-C(2)	1.384(22)	O(1)-C(18)	1.447(23)
C(2)-C(3)	1.353(29)	C(3)-O(4)	1.414(31)
O(4)-C(5)	1.406(26)	C(5)-C(6)	1.454(34)
C(6)-O(7)	1.413(25)	O(7)-C(8)	1.449(30)
C(8)-C(9)	1.424(30)	C(9)-O(10)	1.466(27)
O(10)-C(11)	1.444(21)	C(11)-C(12)	1.525(30)
C(12)-O(13)	1.405(29)	O(13)-C(14)	1.473(27)
C(14)-C(15)	1.461(37)	C(15)-O(16)	1.444(24)
O(16)-C(17)	1.413(33)	C(17)-C(18)	1.482(26)
N-B	1.604(32)	O(19)-C(20)	1.348(70)

Table 5. Bond angles (°) for $BF_3NH_3{\cdot}C_{12}H_{24}O_6{\cdot}CH_2Cl_2$

C(2)-O(1)-C(18)	113.3(4)	O(1)-C(2)-C(3)	110.5(4)
C(2)-C(3)-O(4)	109.7(4)	C(3)-O(4)-C(5)	111.9(4)
O(4)-C(5)-C(6)	109.5(4)	C(5)-C(6)-O(7)	108.0(4)
C(6)-O(7)-C(8)	113.7(3)	O(7)-C(8)-C(9)	108.9(3)
C(8)-C(9)-O(10)	109.4(4)	C(9)-O(10)-C(11)	112.3(3)
O(10)-C(11)-C(12)	110.2(4)	C(11)-C(12)-O(13)	108.5(4)
C(12)-O(13)-C(14)	112.3(3)	O(13)-C(14)-C(15)	108.3(4)
C(14)-C(15)-O(16)	110.4(4)	C(15)-O(16)-C(17)	113.3(3)
O(16)-C(17)-C(18)	109.4(3)	O(1)-C(18)-C(17)	109.0(4)
Cl(1)-C(19)-Cl(2)	112.4(5)	H^a-N-H^b	109.5
H^a-N-H^c	109.5	H^b-N-H^c	109.5
H^a-N-B	103.2(2)	H^b-N-B	105.8(2)
H^c-N-B	119.0(2)	N-B-F(1)	108.4(4)
N-B-F(2)	107.7(4)	F(1)-B-F(2)	109.5(5)
N-B-F(3)	108.3(4)	F(1)-B-F(3)	111.4(4)
F(2)-B-F(3)	111.3(4)		

Table 6. Bond angles (°) for $BH_3NH_3{\cdot}C_{12}H_{24}O_6{\cdot}MeOH$

C(2)-O(1)-C(18)	112.9(13)	O(1)-C(2)-C(3)	108.0(17)
C(2)-C(3)-O(4)	113.2(19)	C(3)-O(4)-C(5)	122.6(16)
O(4)-C(5)-C(6)	113.7(18)	C(5)-C(6)-O(7)	111.8(19)
C(6)-O(7)-C(8)	115.1(17)	O(7)-C(8)-C(9)	107.2(20)
C(8)-C(9)-O(10)	110.0(19)	C(9)-O(10)-C(11)	112.3(14)
O(10)-C(11)-C(12)	107.5(16)	C(11)-C(12)-O(13)	107.2(18)
C(12)-O(13)-C(14)	112.9(16)	O(13)-C(14)-C(15)	109.2(18)
C(14)-C(15)-O(16)	105.5(20)	C(15)-O(16)-C(17)	108.2(18)
O(16)-C(17)-C(18)	112.7(20)	O(1)-C(18)-C(17)	108.3(16)

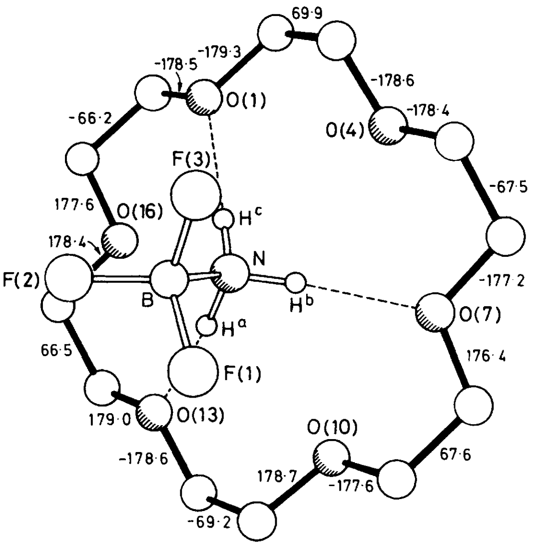

Figure 1. Crystal structure of $BF_3NH_3{\cdot}C_{12}H_{24}O_6{\cdot}CH_2Cl_2$. Torsional angles: |O-C-C-O|, 66.2—69.9(4)°; |C-C-O-C|, 176.4—179.3(4)°. Hydrogen-bond distances *R*[N···O] (Å), *R*[H···O] (Å), angles (θ_N and θ_H°) between COC planes and (*a*) NO vectors and (*b*) HO vectors, N-H···O angles (°) at H atoms: [N···O(1)] 2.95, [H^c···O(1)] 2.01, (*a*) 22, (*b*) 26, H^c 166; [N···O(7)] 2.92, [H^b···O(7)] 1.97, (*a*) 17, (*b*) 17, H^b 177; [N···O(13)] 2.93, [H^a···O(13)] 1.98, (*a*) 20, (*b*) 18, H^a 170. Non-bonded [N···O] (Å) distances: [N···O(4)] 3.10, [N···O(10)] 3.12, and [N···O(16)] 3.14

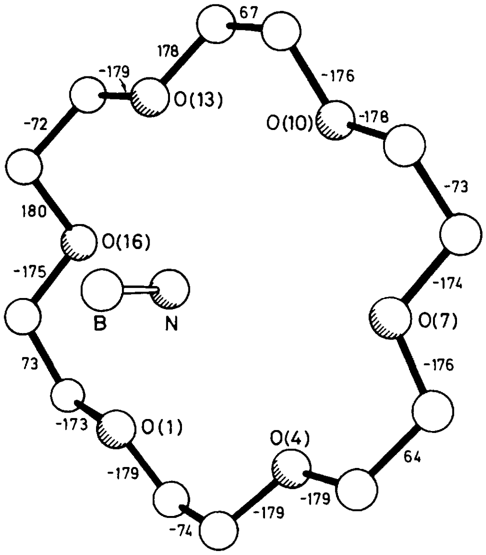

Figure 2. Crystal structure of $BH_3NH_3{\cdot}C_{12}H_{24}O_6{\cdot}MeOH$. Torsional angles: |O-C-C-O|, 64—74°; |C-C-O-C|, 173—180°. Hydrogen-bond distances, *R*[N···O] (Å), angle (θ_N) between COC planes and NO vectors: [N-O(1)] 2.99, 26; [N-O(7)] 3.01, 17; [N-O(13)] 3.02, 17. Non-bonded [N···O] (Å) distances: [N···O(4)] 3.19, [N···O(10)] 3.25, and [N···O(16)] 3.18

compounds to form 1 : 1 complexes with 18-crown-6 is not surprising. Cationic repulsion presumably renders the arrangement of two BX_3NH_3 molecules on opposite faces of 18-crown-6 unstable. In fact, there are no close approaches to the non-complexed face of the crown in either structure. Also, the formation of 1 : 1 complexes does not produce in either case any significant asymmetry in the hosts, which adopt the characteristic all-*gauche* conformations with pseudo D_{3d} symmetry. The N-H···O hydrogen bonding is directly to the upper triangle of oxygen atoms in 18-crown-6 in both structures. This so-called[4] perching arrangement is also characteristic of 1 : 1 complexes involving NH_3Me^+, $NH_3(CH_2COPh)^+$, and $NH_3(CH_2Ph)^+$ ions. The N-H···O hydrogen bonds in $BF_3NH_3{\cdot}C_{12}H_{24}O_6{\cdot}CH_2Cl_2$ are nearly linear with N–H · · · O angles in the range 166—177°. Although the N–H · · · O hydrogen bonds are all slightly longer in $BH_3NH_3{\cdot}C_{12}H_{24}O_6{\cdot}MeOH$, the differences may not be significant in view of the limited accuracy attained for this structure. In $BF_3NH_3{\cdot}C_{12}H_{24}O_6{\cdot}CH_2Cl_2$, the three fluorine atoms on boron are definitely staggered with respect to the three hydrogen atoms on nitrogen. Comparison of the structural data with that published [11] for BF_3NH_3 indicates that geometrical parameters are little changed in the complex. It is interesting, as well as being highly relevant to the origin of the present investigation, to note the structural evidence in this previous paper [11] for intermolecular N–H · · · F hydrogen bonding which, it was proposed, accounts for the involatile character of BF_3NH_3.

Finally, one further structural feature, and one potential chemical property of the new complexes deserve mention. (*i*) Although the structural arrangement and binding in both complexes is essentially the same and the unit-cell parameters are very similar, the complexes are *not* isostructural as indicated by the fact that their space groups are different. The explanation for this difference arises from the different positional relationships of the solvent molecules and 18-crown-6 which result in different packing arrangements in the two complexes. (*ii*) The ability of 18-crown-6, and presumably other crown ethers, to complex with BH_3NH_3 and possibly other borane–ammines provides an opportunity to control and modify the reactivity of this important class of reducing agents towards appropriate organic substrates.

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