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Stabilization of $H_2O \cdot BF_3$ by Hydrogen Bonding to 18-Crown-6

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Abstract. The decomposition of $H_2O \cdot BF_3$ in both the solid and solution states is rapid at room temperature, but 18-crown-6 · $H_2O \cdot BF_3$, **1**, is stable to its melting point, 72°C. **1** crystallizes in the monoclinic space group $C2/c$ with $a = 27.273(9)$, $b = 8.432(5)$, $c = 22.936(9)$ Å, $\beta = 128.33(4)°$, and $D_c = 1.27 \text{ g cm}^{-3}$ for $Z = 8$. Least-squares refinement based on 1409 observed reflections led to a final $R = 0.083$. The BF_3 is covalently bonded to the oxygen atom of the water molecule which in turn is hydrogen bonded to the 18-crown-6.

Key words. Hydrogen bonding, 18-crown-6, boron trifluoride, water, crystal structure.

Supplementary Data relating to this article are deposited with the British Library as supplementary publication No. SUP 82095 (10 pages).

1. Introduction

Although BF_3 is one of the strongest known Lewis acids, its adducts with water are rather unstable. The solid adduct, $H_2O \cdot BF_3$, melts at 10.2°C and evolution of BF_3 occurs from the partially ionized aqueous solution at 20°C [1]. Macrocyclic ligands have previously been used to stabilize numerous otherwise unobtainable or uncharacterizable species through either primary [2] or secondary [3] sphere coordination, and we here report an interesting stabilization of $H_2O \cdot BF_3$.

2. Experimental

2.1. PREPARATION OF 18-CROWN-6 · $H_2O \cdot BF_3$

A mixture of 18-crown-6 (0.24 g, 0.9 mmol), $AgBF_4$ (0.18 g, 1 mmol), and $(\eta^5\text{-}C_5H_5)_2TiCl_2$ (0.23 g, 0.9 mmol) was heated in toluene (10 mL) containing 0.16 g H_2O (0.9 mmol) at 100–110°C for 4 h. The solid material went into solution upon heating and non-crystalline beige-colored material precipitated. The resultant red solution was filtered while hot and left to cool at 0°C overnight upon which colorless crystals were obtained from the red solution. (18-Crown-6 · $H_2O \cdot BF_3$: mp, 72°C; ^{1}H NMR in toluene, 10.0δ(broad singlet, 2H), 3.80δ(sharp singlet, 24H)).

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2.2. X-RAY DATA COLLECTION AND STRUCTURE DETERMINATION

Crystals were mounted in thin-walled glass capillaries under an inert atmosphere. Lattice parameters as determined from a least-squares refinement of $(\sin \theta/\lambda)^2$ values for 24 accurately centered reflections are given in Table I.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the $\omega/2\theta$ scan technique. A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Initial structure solution was effected with the aid of the direct methods program MULTAN which revealed the bulk of the crown ether atoms. Subsequent difference Fourier maps generated using the SHELX system of computer programs readily revealed the remaining non-hydrogen atoms including a solvent molecule of toluene which resides upon a crystallographic center of inversion (the molecule suffering from the requisite two-fold disorder). Full matrix least-squares refinement with isotropic thermal parameters converged at $R = 0.14$. Further refinement with all atoms anisotropic led to $R = 0.096$ and a difference map was used to locate the hydrogen atoms. These were refined for two cycles of least-squares and then constrained to 'ride' upon the bonded atoms. Further refinement converged at $R = 0.083$ and $R' = 0.074$. The weighting scheme was based on $w = 1/((\sigma F_0)^2 + 0.0001(F_0)^2)$. The final values of the positional parameters are given in Table II.

Examination of a final difference map revealed no residual peaks larger than $0.5\text{e}/\text{Å}^3$, the four largest of which were about the disordered toluene framework. No parameter in the final cycle of refinement shifted by more than 0.1 of its estimated standard deviation.

Table I. Crystal data and summary of data collection for 18-crown-6 $\cdot H_2O \cdot BF_3 \cdot 0.5\ C_6H_5Me$.

Mol. wt.	394.5
Space group	$C2/c$
a (Å)	27.273(9)
b (Å)	8.432(5)
c (Å)	22.936(9)
β (°)	128.33(4)
Cell vol. (Å^3)	4138
Mol. /unit cell	8
D_c (g/cm^3)	1.27
μ (cm^{-1})	1.07
Radiation	MoK_α
Cryst. size (mm)	0.35 × 0.32 × 0.45
Scan width (deg)	$0.80 + 0.2 \tan(\theta)$
Std. reflections	800, 040, 008
Decay	<1%
2θ range (deg)	2–44
Reflections measured	3289
Reflections observed	1409
No. Parameters varied	242
R	0.083
R_w	0.074

Table II. Final fractional coordinates for 18-crown-6 · $H_2O \cdot BF_3 \cdot 0.5\ C_6H_5Me$.

Atom	*x/a*	*y/b*	*z/c*	*U*(eq)
O(1)	0.3136(3)	0.6127(7)	0.4244(3)	0.100(22)
O(2)	0.4102(3)	0.5064(8)	0.4164(3)	0.098(8)
O(3)	0.3907(3)	0.2381(1)	0.3293(4)	0.119(29)
O(4)	0.3064(3)	0.0173(7)	0.3170(3)	0.104(35)
O(5)	0.2071(3)	0.1173(8)	0.3214(4)	0.106(33)
O(6)	0.2325(5)	0.388(1)	0.4075(6)	0.217(31)
O(7)	0.3534(2)	0.2493(5)	0.4276(2)	0.074(7)
C(1)	0.3758(5)	0.677(1)	0.4659(6)	0.096(26)
C(2)	0.3969(5)	0.663(1)	0.4193(6)	0.101(12)
C(3)	0.4396(5)	0.484(2)	0.3802(6)	0.135(47)
C(4)	0.4459(6)	0.306(2)	0.3745(7)	0.151(68)
C(5)	0.3935(6)	0.065(1)	0.3234(6)	0.129(24)
C(6)	0.3269(7)	0.004(1)	0.2764(6)	0.141(54)
C(7)	0.2443(5)	−0.055(1)	0.2784(5)	0.079(14)
C(8)	0.2230(5)	−0.031(2)	0.3233(6)	0.107(12)
C(9)	0.1881(6)	0.146(2)	0.3671(7)	0.173(19)
C(10)	0.1891(8)	0.304(2)	0.385(1)	0.22[illegible]1)
C(11)	0.2332(7)	0.548(2)	0.4257(7)	0.157(30)
C(12)	0.2949(7)	0.604(2)	0.4676(6)	0.136(28)
F(1)	0.4113(3)	0.2980(6)	0.5536(2)	0.110(37)
F(2)	0.3622(2)	0.0659(5)	0.5086(2)	0.106(17)
F(3)	0.4467(2)	0.1169(8)	0.5172(3)	0.138(41)
B	0.3964(5)	0.178(1)	0.5060(5)	0.079(2)
T(1)	0.0000	0.095(3)	0.7500	0.177(43)
T(2)	0.0466(9)	0.190(3)	0.810(1)	0.202(168)
T(3)	0.048(1)	0.354(3)	0.811(1)	0.237(157)
T(4)	0.0000	0.426(5)	0.7500	0.206(102)
T(5)A	0.0000	0.588(6)	0.7500	0.207(25)
T(5)B	0.0000	−0.055(6)	0.7500	0.200(22)

3. Results and Discussion

During the course of the reaction of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ with $AgBF_4$ in a toluene solution of 18-crown-6, colorless crystals of 18-crown-6 · $H_2O \cdot BF_3$ were isolated. The source of the H_2O is presumed to be moist 18-crown-6. We have not been able to isolate the title compound from the reaction of $H_2O \cdot BF_3$ with 18-crown-6 in toluene, but the stoichiometric reaction of $(\eta^5\text{-}C_5H_5)_2TiCl_2$, $AgBF_4$, 18-crown-6, and H_2O in toluene affords crystalline 18-crown-6 · $H_2O \cdot BF_3$.

The view of the molecule presented in Figure 1 shows the hydrogen bonding of the $H_2O \cdot BF_3$ to 18-crown-6. The O···O separations of 2.76 and 2.80 Å are typical of hydrogen bonded species [4], as are the O—H, O···H, and O—H···O parameters, 1.31 Å, 1.48 Å, and 172° (average), respectively. The geometry of the $H_2O \cdot BF_3$ moiety is very similar to that observed for $H_2O \cdot BF_3$ in the solid state [5], B—O, 1.53(1) vs. 1.532(6) Å, and B—F, 1.35(1) vs. 1.39(1) Å, respectively (Table III). The contraction of the B—F length in the title compound, while on the borderline of significance, may be attributed to the lack of hydrogen bonding for

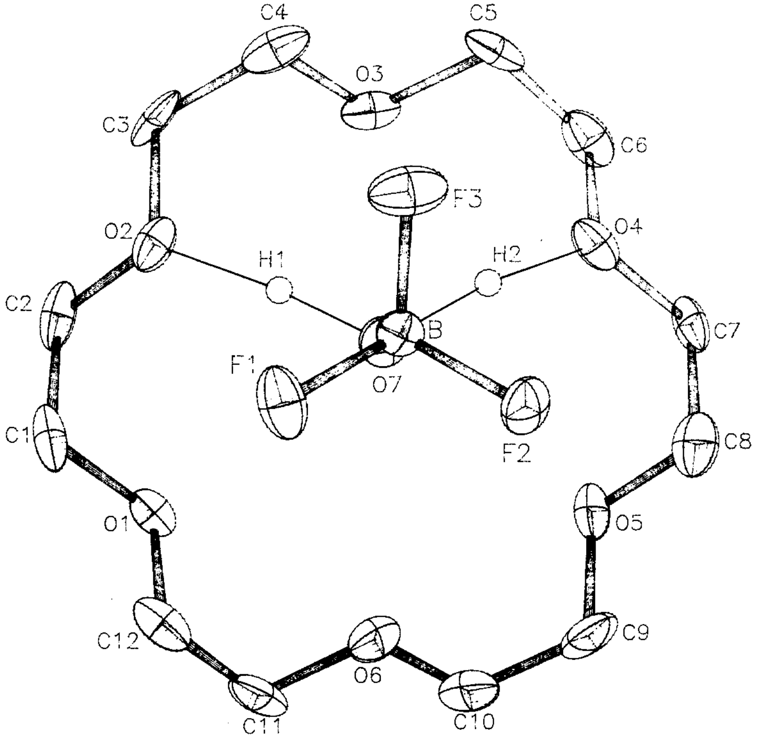
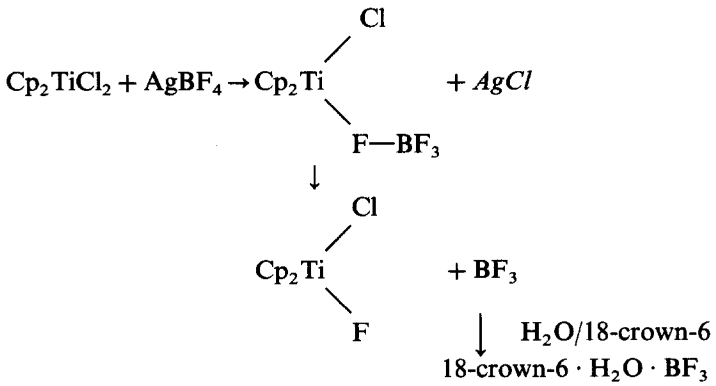


Fig. 1. X-ray structure and atom numbering scheme for 18-crown-6 · H_2O · BF_3, 1.

the fluorine atoms in 18-crown-6 · H_2O · BF_3 as opposed to an extensive hydrogen bonding network in $H_2O \cdot BF_3$ (similar values were also found for $(H_2O)_2 \cdot BF_3$ [6]).

The presence of $H_2O \cdot BF_3$ associated with a copper complex has been reported [7]. Unfortunately, disorder and/or partial occupancy prevented a description of the $H_2O \cdot BF_3$ species. It is worth noting that this species was apparently formed by the hydrolysis of BF_4^-. We can offer two more detailed possibilities for the formation of the title compound:

1.

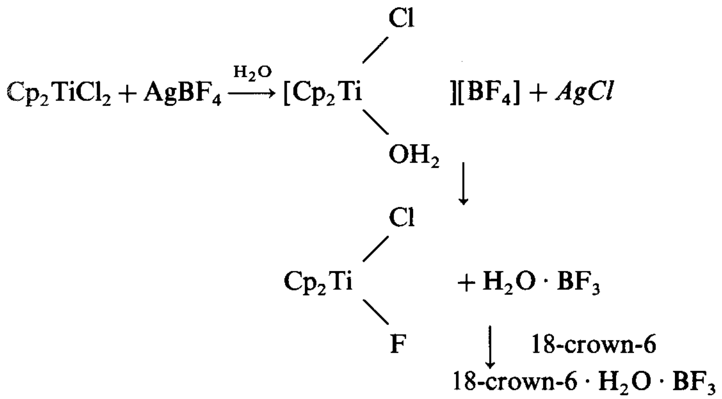


$$Cp_2TiCl_2 + AgBF_4 \rightarrow Cp_2Ti\begin{matrix} \diagup Cl \\ \diagdown F{-}BF_3 \end{matrix} + \mathit{AgCl}$$

$$\downarrow$$

$$Cp_2Ti\begin{matrix} \diagup Cl \\ \diagdown F \end{matrix} \quad + BF_3 \xrightarrow{H_2O/18\text{-crown-6}} 18\text{-crown-6} \cdot H_2O \cdot BF_3$$

2.



The formation of $Cp_2Ti(Cl)F$ has a precedent, as may be seen in the work of Jordan [8]:

$$Cp_2Zr(Me)Cl + AgPF_6 \xrightarrow{CH_3CN} [Cp_2Zr(Me)(CH_3CN)][PF_6] + \mathit{AgCl}$$
$$\downarrow$$
$$Cp_2Zr(Me)F + PF_5$$

Table III. Bond lengths (Å) and angles (°) for **1**.

Atoms	Distance	Atoms	Distance
O(1)—C(1)	1.44(1)	O(1)—C(12)	1.37(1)
O(2)—C(2)	1.38(1)	O(2)—C(3)	1.48(1)
O(3)—C(4)	1.32(1)	O(3)—C(5)	1.47(1)
O(4)—C(6)	1.35(1)	O(4)—C(7)	1.47(1)
O(5)—C(8)	1.32(1)	O(5)—C(9)	1.45(1)
O(6)—C(10)	1.19(2)	O(6)—C(11)	1.41(1)
O(7)—B	1.53(1)	C(1)—C(2)	1.50(1)
C(3)—C(4)	1.52(1)	C(5)—C(6)	1.52(1)
C(7)—C(8)	1.48(1)	C(9)—C(10)	1.39(2)
C(11)—C(12)	1.41(1)	B—F(1)	1.35(1)
B—F(2)	1.36(1)	B—F(3)	1.33(1)

Atoms	Angle	Atoms	Angle
C(1)—O(1)—C(12)	110.8(9)	C(2)—O(2)—C(3)	113.4(9)
C(4)—O(3)—C(5)	114(5)	C(6)—O(4)—C(7)	111.4(8)
C(8)—O(5)—C(9)	113(1)	C(10)—O(6)—C(11)	122(1)
O(1)—C(1)—C(2)	108.3(9)	O(2)—C(2)—C(1)	109.8(9)
O(2)—C(3)—C(4)	107.6(8)	O(3)—C(4)—C(3)	111(1)
O(3)—C(5)—C(6)	107.2(8)	O(4)—C(6)—C(5)	107.8(9)
O(4)—C(7)—C(8)	109.2(8)	O(5)—C(8)—C(7)	112(1)
O(5)—C(9)—C(10)	115(1)	O(6)—C(12)—C(9)	122(2)
O(6)—C(11)—C(12)	108(1)	O(1)—C(12)—C(11)	110(1)
O(7)—B—F(1)	106.3(7)	F(1)—B—F(2)	110.8(7)
O(7)—B—F(2)	106.2(7)	F(1)—B—F(3)	112.0(9)
F(2)—B—F(3)	112.2(8)	O(7)—B—F(3)	109.0(7)

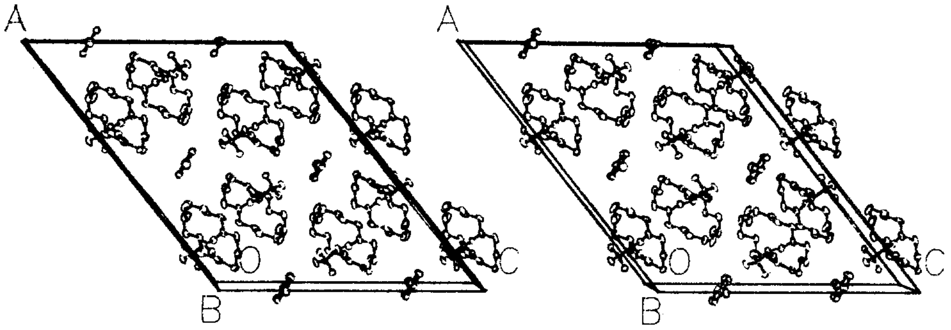


Fig. 2. Stereoscopic view of the unit cell packing for 1 · 0.5 C_6H_5Me.

The oxygen atoms of the crown are planar to within 0.23 Å, in keeping with 0.20 Å in [H_3O · 18-crown-6][Cl—H—Cl] [9] and 0.23 Å in [H_3O · 18-crown-6][H_5O_2 · 2 Cl] [10].

The compound crystallized with 0.5 toluene per molecule of complex. As can be seen in Figure 2, the toluene molecules lie in channels bounded by the complex host molecules.

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References

1. F. A. Cotton and G. Wilkinson: *Advanced Inorganic Chemistry*, 4th Ed., Interscience, New York (1980), p. 233.
2. S. G. Bott, A. Alvanipour, S. D. Morley, D. A. Atwood, A. W. Coleman, and J. L. Atwood: *Angew. Chem. Int. Ed. Engl.* **26**, 485 (1987).
3. H. M. Colquhoun, J. F. Stoddart, and D. J. Williams: *Angew. Chem. Int. Ed. Engl.* **25**, 487 (1986).
4. A. Elbasyouny, J. J. Brugge, K. von Deuten, M. Dickel, A. Knochel, K. U. Koch, D. Melzer, and G. Rudolph: *J. Am. Chem. Soc.* **105**, 6568 (1983).
5. D. Mootz and M. Steffen: *Z. Anorg. Allg. Chem.* **483**, 171 (1981).
6. D. Mootz and M. Steffen: *Acta Crystallogr.* **B37**, 1110 (1981).
7. J. van Rijn, J. Reedijk, M. Dartmann, and B. Krebs: *J. Chem. Soc., Dalton Trans.* 2579 (1987).
8. R. F. Jordan, W. E. Dasher, and S. F. Echols: *J. Am. Chem. Soc.* **108**, 1719 (1986).
9. J. L. Atwood, S. G. Bott, A. W. Coleman, K. D. Robinson, S. B. Whetstone, and C. M. Means: *J. Am. Chem. Soc.* **109**, 8100 (1987).
10. J. L. Atwood, S. B. Bott, K. D. Robinson, M. T. May, and E. J. Bishop: *Angew. Chem. Int. Ed. Engl.*, submitted.