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REACTIONS OF TRIPHENYLARSINE OXIDE WITH AQUEOUS HYDROGEN FLUORIDE: CRYSTAL STRUCTURE OF BIS(TRIPHENYLARSINE OXIDE)HYDROGEN(I) TETRAFLUOROBORATE

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SUMMARY

Fluorination of triphenylarsine oxide by aqueous hydrogen fluoride (1-40%) in the absence of glass readily gives triphenylarsine difluoride. When the reaction with dilute (1%) aqueous hydrogen fluoride is carried out in borosilicate glass apparatus, the glass participates in the reaction resulting in the formation of the crystalline 2:1 adduct $2Ph_3AsO.HBF_4$. Crystals of this compound are monoclinic, $\underline{P}2_1/\underline{c}$, $\underline{a}$ = 12.926(4), $\underline{b}$ = 17.819(6), $\underline{c}$ = 14.994(4) Å, β = 98.97(3)°, Z = 4. The structure contains cations $[(Ph_3AsO)_2H]^+$ in which O···O is 2.44(2)Å, and anions BF_4^-.

INTRODUCTION

The reactions of triphenylarsine oxide with aqueous solutions of hydrogen fluoride have been studied in an attempt to prepare triphenylarsine oxide-hydrogen fluoride ($Ph_3AsO.HF$). We have previously reported that the reaction of 40% hydrofluoric acid gives triphenylarsine difluoride in good yield [1]; it has now been found that two compounds can be isolated from the system triphenylarsine oxide - aqueous hydrogen fluoride, and that they are interconvertible.

RESULTS AND DISCUSSION

When the reaction between triphenylarsine oxide and aqueous hydrogen fluoride in the cencentration range 1-40% is carried out in plastic (polypropylene or polyethylene) vessels, the product is triphenylarsine difluoride. When this reaction is carried out in a glass (Pyrex) vessel using 40% hydrofluoric acid, triphenylarsine difluoride is again the product. However, use of 1% hydrofluoric acid in glass did not yield triphenylarsine difluoride, but gave, in good yield, a white crystalline compound (I) for which elemental analysis (C,H,As,B,F) suggested a composition corresponding to a 2:1 additon compound $2Ph_3AsO.HBF_4$.

This product is soluble in acetonitrile yielding solutions of high molar conductance. Its infra-red spectrum contains features found in the spectra of compounds containing the strongly hydrogen bonded ion $[(Ph_3AsO)_2H]^+$ (these include the presence of a strong, very broad absorption in the range 1600-600 cm^{-1} [2] and the absence of any band due to OH stretching above 1700 cm^{-1}); a strong peak at 1058 cm^{-1} is close to the main peak found in the infra-red spectra of alkali metal tetrafluoroborates (ν_3 at 1050 cm^{-1}) [3].

In addition, the n.m.r. spectra of compound (I) provided strong evidence for the presence of BF_4^- ions. The ^{19}F spectrum in anhydrous CD_3CN showed a single absorption at δ -151.0 p.p.m., relative to CCl_3F: corresponding shifts for BF_4^- in pentane and in liquid hydrogen fluoride solutions are -150.4 p.p.m. [4] and -153.6 p.p.m. [5] respectively. The ^1H spectrum contains two absorptions at δ 7.67 p.p.m. (multiplet) and 15.02 p.p.m. (singlet) with an integral ratio of 30:1, consistent with the formulation of the cation as $[(Ph_3AsO)_2H]^+$: in damp CD_3CN, the 15.02 p.p.m. resonance disappears, and is replaced by a broad absorption centred at 9.85 p.p.m., indicating hydrolysis of the cation to $(Ph_3AsOH)^+$.

An authentic sample of $2Ph_3AsO.HBF_4$, prepared directly from triphenylarsine oxide and fluoroboric acid, in polypropylene apparatus, was found to be identical with (I).

An X-ray crystal structure analysis confirmed that (I) has a structure consisting of the ions $[(Ph_3AsO)_2H]^+$ (Figure 1) and BF_4^-. In the cation, the unique hydrogen was not located by the X-ray data, possibly because of its close proximity to the two arsenic atoms: however, its presence is shown, not only by the infra-red and n.m.r. spectra discussed above, but by the very short, strongly hydrogen bonded O⋯O distance, 2.436Å.

Novak has presented a smooth correlation between OH stretching frequency and O⋯O distance in species containing OHO fragments [6], in terms of which an O⋯O distance of 2.436Å is associated with a stretching frequency of ca 800 cm^{-1}, consistent with the present observations. Although the cation does not lie across a centre of inversion, it seems quite possible that the OHO fragment is symmetrical, since very many short OHO bonds have been found to span inversion centres [7]. Similarly, a linear relationship has been demonstrated [6] between OH stretching frequency and OH distance in such fragments, and a frequency of 800 cm^{-1} implies, on this basis, an OH distance of ca 1.22Å. Such a distance in turn is consistent with the presence of a symmetric, linear OHO fragment in the cation $[(Ph_3AsO)_2H]^+$.

It is clear from the formation of $[(Ph_3AsO)_2H]BF_4$ that there is active participation of the borosilicate glass vessel in the reaction leading to (I) as it is well known that hydrofluoric acid reacts with both boric acid and borates to yield fluoroboric acid:

$$8HF + B_2O_3 \longrightarrow 2H_3O^+BF_4^- + H_2O$$

The present work shows that for the reaction of 40% hydrofluoric acid in either glass or plastic vessels, and for 1% acid in plastic, the main reaction with triphenylarsine oxide is fluorination:

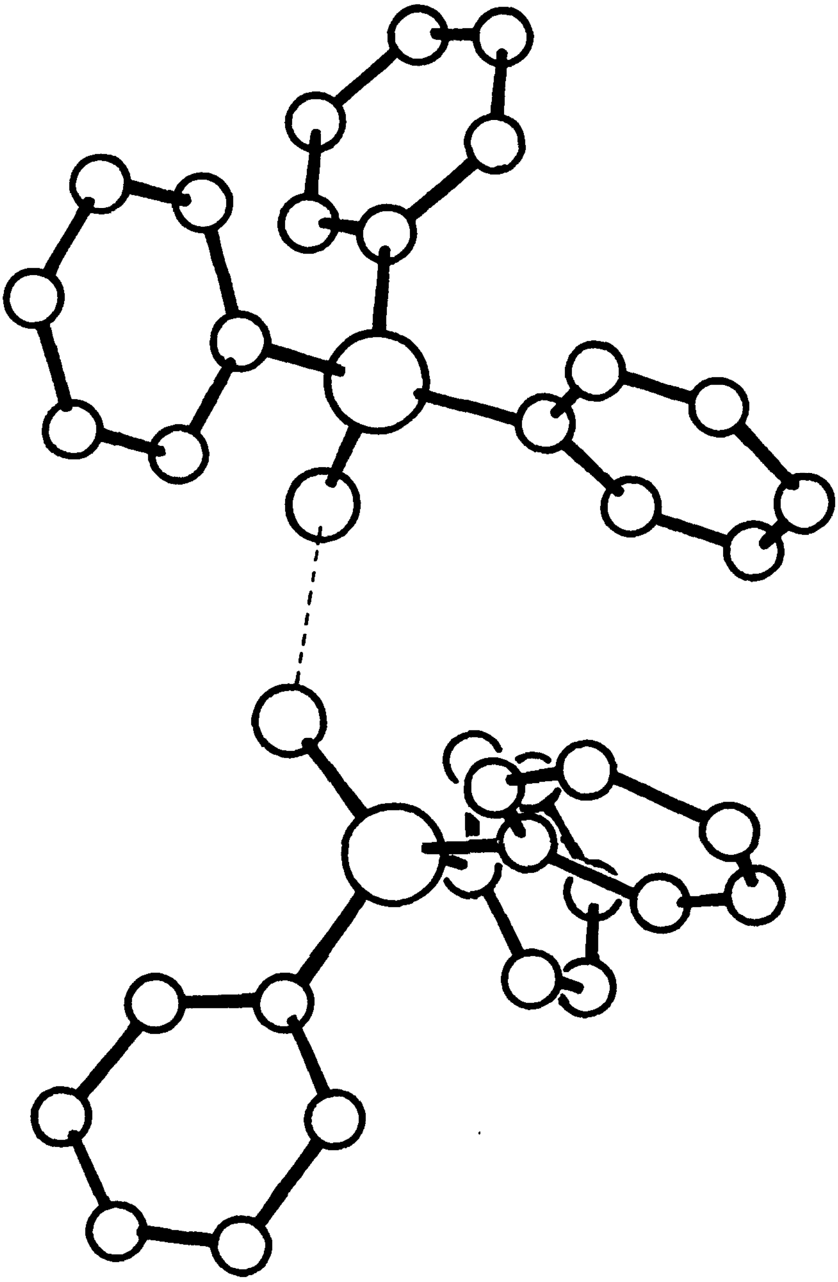

Fig. 1 The cation $[(Ph_3AsO)_2H]^+$: hydrogen atoms are not shown.

$$Ph_3AsO + 2HF \longrightarrow Ph_3AsF_2 + H_2O$$

while the reaction with 1% hydrofluoric acid in glass may be written:

$$2Ph_3AsO + H_3O^+BF_4^- \longrightarrow \underset{(I)}{[(Ph_3AsO)_2H]BF_4} + H_2O$$

We have in addition shown that the reaction of (I) with 40% hydrofluoric acid in plastic vessels leads to triphenylarsine difluoride:

$$4HF + [(Ph_3AsO)_2H]BF_4 \longrightarrow 2Ph_3AsF_2 + H_3O^+BF_4^- + H_2O$$

and that triphenylarsine difluoride can in turn be converted to (I) by reaction, in the absence of glass, with 1% fluoroboric acid:

$$2Ph_3AsF_2 + H_3O^+BF_4^- + H_2O \longrightarrow [(Ph_3AsO)_2H]BF_4 + 4HF$$

These interconversions account for the absence of (I) from the products of the reaction of triphenylarsine oxide with the 40% acid, and show that any difluoride formed by action of the 1% acid in glass, will be converted to (I) by further reaction with fluoroboric acid. In the absence of glass, and hence of fluoroboric acid, the sole product is the difluoride.

In the course of the interconversions of Ph_3AsF_2 and $[(Ph_3AsO)_2H]BF_4$ in aqueous media, no $[Ph_3AsOH]BF_4$ was isolated, even though hydrolysis of the ion $[(Ph_3AsO)_2H]^+$ in acetonitrile solution gives $[Ph_3AsOH]^+$. In acetonitrile the system is homogeneous, whereas the aqueous reactions are heterogeneous processes in which most if not all of the arsenic-containing species are in the solid state throughout. Previous attempts to isolate the salt $[Ph_3AsOH][BF_4]$ have been unsuccessful [8], and it appears that while these two ions may co-exist in solution, attempts to precipitate them as a solid salt cause conversion to other compounds, such as $[(Ph_3AsO)_2H]BF_4$ or $Ph_3AsO.BF_3$.

EXPERIMENTAL

General

Standard reagents of the best commercial grade available were used and, if necessary, purified by conventional methods. Triphenylarsine oxide was prepared by a standard method [9]. Purification of acetonitrile for conductance measurements was carried out by the method described by Smith and Witten [10].

Conductance measurements were made in a small dipping electrodes cell and values of conductance were obtained using a Wayne Kerr univeral bridge (B641). Infra-red spectra were recorded as nujol and voltalef(3S) mulls using a Perkin Elmer 257 infra-red spectrophotometer. ^{19}F and ^{1}H n.m.r. spectra were measured at 75MHz and 80MHz respectively on a Bruker NP-80 n.m.r. spectrometer. Mass spectra were recorded at 70eV using an A.E.I. MS902 instrument. Microanalyses were carried out by A. Bernhardt, Max Planck Institut, Mulheim, Germany, (As,B,F) and S. Smith, Chemistry Department, University of St. Andrews (C,H).

Reaction between triphenylarsine oxide and hydrofluoric acid (1%) in a glass vessel

Triphenylarsine oxide monohydrate (0.51 g, 1.50 mmol) and hydrofluoric acid (1%; 20 ml, 10 mmol) were shaken together in a Pyrex flask for 24 hours, after which the flask contained a finely divided solid in a frothy mother liquor. Filtration, washing with distilled water, and drying under vacuum gave $[(Ph_3AsO)_2H]BF_4$ (0.30 g, 28%). Recrystallisation from water/ethanol gave white needles, m.p.168-170°. Mixed m.p. with an authentic specimen of $[(Ph_3AsO)_2H]BF_4$ prepared from the reaction between Ph_3AsO and aqueous HBF_4 was 168-170°. (Found: C, 58.8; H, 4.1; As, 20.7; B, 1.5; F, 10.3. $C_{36}H_{31}As_2BF_4O_2$ requires C, 59.0; H, 4.3; As, 20.5; B, 1.5; F, 10.4%.) I.r.: 3 050 w, 1 980 vw, 1 960 vw, 1 814 vw, 1 770 vw, 1 577 w, 1 480 m, 1 440 s, 1 340 vw, 1 312 w, 1 285 w, 1 187 m, 1 170 w, 1 100 s, sh, 1 090 s, 1 058 vs, 1 043 s, sh, 1 028 m, sh, 1 000 m, 930 w, sh, 866 m, 848 m, sh, 770 s, 758 s, 748 s, 690 s cm^{-1}. The peaks occurring in the range 1500-625 cm^{-1} are superimposed on a very broad, medium intensity absorption band.

Reaction between triphenylarsine oxide and hydrofluoric acid (40%) in a glass vessel

Triphenylarsine oxide monohydrate (0.65 g, 1.91 mmol) and distilled water (30 ml) were heated to boiling in a Pyrex beaker and stirred magnetically using a P.T.F.E. enclosed stirring bar. Hydrofluoric acid (40%, 20 ml, 400 mmol) was added to the boiling solution resulting in the formation of a white precipitate. The mixture was stirred for a further 45 min after which filtration, washing with water and drying under vacuum gave triphenylarsine difluoride (0.51 g, 78%) m.p. 134-136° (from acetone) (Found: C, 62.9; H, 4.4. Calculated for $C_{18}H_{15}F_2$: C, 62.8; H, 4.4%). I.r.: 3 095 w, 3 060 m, 1 975 vw, 1 915 vw, 1 830 vw, 1 780 vw, 1 682 vw, 1 486 m, 1 480 m, sh, 1 442 vs, 1 397 w, 1 348 w, 1 320 m, 1 188 m, 1 160 w, 1 090 s, 1 083 s, 1 023 m, 1 000 w, 995 w, 980 vw, 930 w, 923 w, sh, 855 w, 751 vs, 745 s, 691 vs. The same product was obtained when this reaction was carried out in a polypropylene vessel.

Reaction between triphenylarsine oxide and hydrofluoric acid (1%) in a plastic vessel

Triphenylarsine oxide monohydrate (0.50 g, 1.47 mmol) was stirred with hydrofluoric acid (1%; 20 ml, 10 mmol) in a polypropylene beaker for 24 hours after which the beaker contained a finely divided white solid suspended in a frothy liquid. The solid was filtered off, washed with water, and dried under vacuum giving triphenylarsine difluoride (0.44 g, 80%), identified from its m.p. and i.r. spectrum.

Reaction between triphenylarsine oxide and fluoroboric acid

Triphenylarsine oxide monohydrate (0.50 g, 1.47 mmol) was dissolved in water (30 ml) at 90 °C in a polypropylene beaker. Fluoroboric acid solution (40%; 0.4 ml, 1.8 mmol) was added, with stirring, resulting in the immediate precipitation of a white solid. Stirring was maintained as the mixture cooled to room temperature. The product was filtered, washed with water, and dried under vacuum to give $[(Ph_3AsO)_2H]BF_4$ (0.33 g, 61%) m.p. 168-170° (Found: C, 58.6; H, 4.5. $C_{36}H_{31}As_2BF_4O_2$ requires C, 59.0; H, 4.3%).

Reaction between triphenylarsine difluoride and fluoroboric acid

Triphenylarsine difluoride (0.22 g, 0.64 mmol) and fluoroboric acid (1%; 40 ml, 4.6 mmol) were mixed in a polypropylene beaker and stirred for 22 hours. After dilution with water, the mixture was filtered and the white solid obtained washed with water and dried under vacuum giving $[(Ph_3AsO)_2H]BF_4$ (0.06 g, 26%), identical (m.p., i.r. spectrum) with an authentic sample.

Reaction between $[(Ph_3AsO)_2H]BF_4$ and hydrofluoric acid (1%) .

$[(Ph_3AsO)_2H]BF_4$ (0.23 g, 0.31 mmol) and hydrofluoric acid (1%; 40 ml, 20 mmol) were stirred together for 22 hours in a polypropylene beaker. The white solid product was removed by filtration, washed with water, dried under vacuum giving triphenylarsine difluoride (0.17 g, 77%), identical (m.p., i.r. spectrum) with an authentic sample.

Mass spectra

In the spectrum of Ph_3AsF_2, the molecular ion is only very weakly abundant, but was identified unambiguously by accurate mass measurement: the ions at m/e values of 325, 306, 267, 248, 229, 171 and 152 correspond to simple cleavage of phenyl groups and/or fluorine atoms. The ion at m/e 323 $(M-2H-F)^+$ is almost certainly the heterocyclic 9-fluoro-9-phenyl-9-arsafluorenonium ion, while that at m/e 227 $(M-Ph-2H-2F)^+$, is the parent 9-dehydro-9-arsafluorenonium ion: $C_{12}H_8^+$ is the cation of biphenylene. There is a single rearrangement ion $C_6H_5F^+$.

In the spectrum of $[(Ph_3AsO)_2H]BF_4$, two major series of ions can be identified: one series corresponds to the spectrum of Ph_3AsO [11], while the other contains the ions $Ph_2AsF_2^+$, Ph_2AsF^+, and $PhAsF^+$, indicating the formation of fluoro(phenyl)arsenic species. Significantly, no ions are observed which contain both oxygen and fluorine, nor are any fluorine-containing ions (apart from BF_2^+) observed which do not occur in the spectrum of Ph_3AsF_2. It is probable that under the conditions prevailing in the spectrometer inlet system (250 °C/ 10^{-6} torr), $[(Ph_3AsO)_2H]BF_4$ is thermally decomposed by two routes to give as the major volatile species Ph_3AsO and Ph_3AsF_2, so that its mass spectrum is essentially a superimposition of the spectra of these two compounds. (Details of the spectra are available from the authors on request.)

In a separate pyrolysis experiment carried out at 250 °C/ 10^{-3} torr, the identified (i.r.) pyrolysis products of $[(Ph_3AsO)_2H]BF_4$ were Ph_3AsO, $Ph_3AsO.BF_3$, and Ph_3AsF_2. The ease of fluorination of Ph_3AsO to Ph_3AsF_2 is thus again demonstrated.

X-ray measurements

The intensities of 4894 unique reflections having $2° \leqslant \theta \leqslant 30°$ in the quadrant $\pm \underline{h}$, $+\underline{k}$, $+\underline{l}$ for $\underline{k}$ = 0.19 ($0 \leqslant \mu \leqslant 22.265°$) were measured using a Stoe STADI-2 two circle diffractometer in the ω-2θ scan mode: each scan comprised 120 steps, each of 0.01° in ω, measured for 0.6 s per step: backgrounds were measured at each end of the peak scan for a time of (scan time/2). Standard reflections, measured after every 50 reflections, showed only small random deviations from their means. Lp corrections were applied to the data, but no absorption correction was made.

Crystal data

$C_{36}H_{31}As_2BF_4O_2$, $\underline{M}_r$ = 732.29; monoclinic, space-group $\underline{P}2_1/\underline{c}$, ($C_{2h}^5$, No.14); $\underline{a}$ = 12.926(4), $\underline{b}$ = 17.819(6), $\underline{c}$ = 14.994(4)Å; β = 98.87(3)°; μ = 3412.2Å^3; Z = 4; D_c = 1.410 kg dm^{-3}; graphite monochromatised Mo-Kα radiation, λ = 0.71069Å, μ(Mo-Kα) = 19.32 cm^{-1}.

Structure solution and refinement

The structure was solved by direct methods using SHELX-76 [12] and refined with As,F,O,C and B anisotropic, and a common isotropic temperature parameter for phenyl hydrogens in calculated positions to give R = 0.106 and R_G = 0.119 for 2497 reflections having $I \geqslant 3\sigma(I)$. A final difference map failed to find the unique hydrogen atom in the cation but otherwise showed no unexpected features.

Final atom coordinates are in Table 2 and the geometry of the $C_3AsO \cdots OAsC_3$ core of the $(Ph_3AsOHOAsPh_3)^+$ cation is given in Table 1 (Full details of the cation geometry, the anisotropic temperature factors and the observed and calculated structure factors are available upon request.) The cation is shown in Figure 1.

The thermal motion of the BF_4^- group was very large and very anisotropic, and the inter-atomic distances calculated from the refined positional coordinates were very short. Analysis of the thermal motion by the method of Schomaker and Trueblood [13] yielded the corrections to the distances shown in Table 3. The thermal analysis correction increases the refined value of the mean B-F distance from 1.313Å to 1.461Å: previous X-ray determinations have yielded values of 1.377Å (uncorrected) in $NaBF_4$ [14], and 1.382Å (uncorrected) and 1.406Å (corrected) in NH_4BF_4 [16]: a study of ^{19}F spin-lattice relaxation in MBF_4 (M = Na,K,Rb,Cs) yielded a range of B-F distances from 1.410(15)Å in KBF_4 to 1.445(15)Å in $CsBF_4$, with mean 1.425(15)Å [15]. In the present study the correction is large, and the corresponding half-amplitudes for libration about the three independent axes are 17.0°, 18.2°, and 21.8°.

TABLE 1

Geometry of the $C_3AsO \cdots OAsC_3$ core in the $(Ph_3AsOHOAsPh_3)^+$ cation

As(1)-O(1)	1.672(15)Å	As(2)-O(2)	1.679(15)Å
As(1)-C(111)	1.869(20)	As(2)-C(211)	1.913(22)
As(1)-C(121)	1.910(19)	As(2)-C(221)	1.923(19)
As(1)-C(131)	1.911(24)	As(2)-C(231)	1.884(22)
O(1)···O(2)	2.436(21)		
O(1)-As(1)-C(111)	106.8(8)°	O(2)-As(2)-C(211)	109.0(8)°
O(1)-As(1)-C(121)	111.9(8)	O(2)-As(2)-C(221)	110.8(8)
O(1)-As(1)-C(131)	110.3(8)	O(2)-As(2)-C(231)	105.1(8)
C(111)-As(1)-C(121)	107.5(9)	C(211)-As(2)-C(221)	112.5(9)
C(121)-As(1)-C(131)	111.7(9)	C(221)-As(2)-C(231)	109.0(9)
C(131)-As(1)-C(111)	108.5(9)	C(231)-As(2)-C(211)	110.2(9)
As(1)-O(1)-O(2)	129.6(8)	As(2)-O(2)-O(1)	115.1(8)
As(1)-O(1)-O(2)-As(2)	99.5(2)		

TABLE 2

Fractional atomic coordinates (x 10^4)

Atom	*x*	*y*	*z*
F(1)	6626(28)	3323(17)	3938(13)
F(2)	7610(16)	4144(14)	4711(19)
F(3)	7233(24)	3067(15)	5303(15)
F(4)	6052(19)	3921(21)	4955(20)
B	6883(22)	3641(20)	4733(20)
As(1)	3204(2)	3296(1)	8991(1)
O(1)	2087(11)	3774(8)	8971(9)
C(111)	3840(15)	3662(11)	8040(12)
C(112)	4409(18)	3171(13)	7547(12)
C(113)	4867(19)	3433(17)	6759(15)
C(114)	4693(20)	4153(16)	6537(16)
C(115)	4135(20)	4654(14)	6989(15)
C(116)	3705(19)	4376(15)	7728(13)
C(121)	4152(16)	3464(12)	10083(13)
C(122)	3777(17)	3730(13)	10837(13)
C(123)	4481(25)	3823(16)	11618(15)
C(124)	5541(23)	3608(16)	11718(16)
C(125)	5861(16)	3371(14)	10957(16)
C(126)	5180(19)	3276(14)	10147(18)
C(131)	2918(18)	2252(14)	8792(15)
C(132)	2041(22)	2017(20)	8273(20)
C(133)	1752(25)	1356(22)	8104(24)
C(134)	2447(28)	771(20)	8494(21)
C(135)	3379(24)	974(15)	9043(18)
C(136)	3638(18)	1706(15)	9212(14)
As(2)	27(2)	3436(1)	10180(1)
O(2)	1066(11)	4002(8)	10181(9)
C(211)	503(17)	2421(13)	10338(14)
C(212)	-182(19)	1831(15)	9960(16)
C(213)	217(29)	1145(19)	10100(26)
C(214)	1205(27)	977(19)	10552(18)
C(215)	1831(23)	1561(19)	10920(19)
C(216)	1455(20)	2252(18)	10798(18)
C(221)	-965(15)	3570(14)	9097(14)
C(222)	-557(19)	3606(15)	8263(17)
C(223)	-1284(27)	3738(15)	7492(16)
C(224)	-2328(28)	3747(21)	7496(18)
C(225)	-2693(21)	3680(27)	8282(20)
C(226)	-2001(21)	3602(22)	9098(20)
C(231)	-591(16)	3745(13)	11178(14)
C(232)	-1054(19)	3205(12)	11674(13)
C(233)	-1515(20)	3414(14)	12464(13)
C(234)	-1490(19)	4121(16)	12688(17)
C(235)	-1057(23)	4702(16)	12184(20)
C(236)	-629(22)	4454(16)	11442(17)

TABLE 3

Distances in the BF_4^- anion (Å)

	uncorrected	corrected for libration	
B-F(1)	1.314(38)	1.471	mean 1.461
B-F(2)	1.302(40)	1.434	
B-F(3)	1.364(41)	1.500	
B-F(4)	1.274(42)	1.439	
F(1)····F(2)	2.155(38)	2.417	mean 2.383
F(1)····F(3)	2.125(31)	2.331	
F(1)····F(4)	2.088(43)	2.346	
F(2)····F(3)	2.199(38)	2.394	
F(2)····F(4)	2.138(35)	2.371	
F(3)····F(4)	2.161(42)	2.441	

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