Table IV. Selected Interatomic Distances (Å) and Angles (deg)

N(21)–S(11)	1.635 (9)	N(22)–S(12)	1.64 (1)
N(21)–S(31)	1.62 (1)	N(22)–S(32)	1.631 (9)
N(41)–S(31)	1.59 (1)	N(42)–S(32)	1.59 (1)
C(51)–N(41)	1.37 (2)	C(52)–N(42)	1.34 (2)
C(51)–N(61)	1.33 (2)	C(52)–N(62)	1.34 (1)
N(61)–S(11)	1.57 (1)	N(62)–S(12)	1.59 (1)
C(11)–C(51)	1.46 (2)	C(21)–C(52)	1.48 (2)
S(11)–S(32)	2.509 (4)	S(12)–S(31)	2.534 (4)
N(21)–S(11)–N(61)	113.8 (6)	N(42)–C(52)–N(62)	128 (1)
S(11)–N(21)–S(31)	116.3 (7)	N(42)–C(52)–C(21)	114 (1)
N(21)–S(31)–N(41)	114.2 (5)	N(62)–C(52)–C(21)	118 (1)
S(31)–N(41)–C(51)	123 (1)	S(12)–N(62)–C(52)	121.4 (9)
N(41)–C(51)–N(61)	126 (1)	C(52)–C(21)–C(22)	121 (1)
N(41)–C(51)–C(11)	115 (1)	C(52)–C(21)–C(26)	122 (1)
N(61)–C(51)–C(11)	119 (1)	C(51)–C(11)–C(12)	120 (1)
S(11)–N(61)–C(51)	124.9 (9)	C(51)–C(11)–C(16)	123 (1)

atoms were located in difference Fourier maps. The data were corrected for absorption by DIFABS after isotropic refinement.[20] All non-hydrogen atoms were refined anisotropically, with the hydrogens calculated in idealized positions with fixed isotropic temperature factors, which were not refined. The refinement did not converge until the data were limited to the sphere with $(\sin\theta)/\lambda$ less than 0.64. Convergence was reached at $R = 0.084$. The final values of the refined positional parameters are presented in Table III, and important bond lengths are in Table IV. Neutral-atom scattering factors were used with anomalous dispersion corrections applied.[21] No corrections for extinction were made. All calculations were carried out on a Zenith 386 running UNIX V.3 computer at the University of Calgary with the program package XTAL.[22]

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Registry No. **3b**, 139100-95-1; **3c**, 139100-96-2; **3d**, 139100-97-3; **3e**, 139100-98-4; **3f**, 139100-99-5; **3g**, 139101-00-1; **4b**, 139101-01-2; **4c**, 139101-02-3; **4d**, 139101-03-4; **4e**, 139101-04-5; **4f**, 139101-05-6; **4g**, 139101-06-7; **5b**, 139101-07-8; **5c**, 110654-28-9; **5d**, 139101-08-9; **5e**, 139101-09-0; **5f**, 139101-10-3; **5g**, 139101-11-4; **6b**, 139101-12-5; **6c**, 139101-13-6; **6d**, 139101-14-7; **6e**, 139101-15-8; **6f**, 139101-16-9; **6g**, 139101-17-0; $S_3N_3Cl_3$, 18428-81-4; 4-$CH_3C_6H_4CN(SiMe_3)_2NSiMe_3$, 117357-77-4; 4-$ClC_6H_4CN(SiMe_3)_2NSiMe_3$, 117357-78-5; 4-$CF_3C_6H_4CN(SiMe_3)_2NSiMe_3$, 117357-81-0; 4-$CH_3OC_6H_4CN(SiMe_3)_2NSiMe_3$, 117357-79-6; 4-$C_6H_5C_6H_4CN(SiMe_3)_2NSiMe_3$, 117357-82-1; 3-$CF_3C_6H_4CN(SiMe_3)_2NSiMe_3$, 139101-18-1; 1-norbornene, 21810-44-6.

Supplementary Material Available: Tables of hydrogen atom positions and thermal parameters, comprehensive lists of bond distances and angles, and a table of significant contact distances (8 pages); a table of F_o, F_c, and $\sigma(F)$ values (23 pages). Ordering information is given on any current masthead page.

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Tetrakis(pentafluorooxotellurato)borate(1−): Coordinating Ability and Reactivity of a Very Large Weakly Coordinating Anion

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The suitability of $B(OTeF_5)_4^-$ as a counterion for the generation of "coordinatively unsaturated" or weakly solvated metal and metalloid cations has been studied by IR and NMR spectroscopy and by single-crystal X-ray diffraction. Addition of $B(OTeF_5)_3$ to $MOTeF_5$ (M = Ag, Tl) in the weakly coordinating solvents mesitylene, dichloromethane, 1,2-dichloroethane, and 1,1,2-trichlorotrifluoroethane produces solutions of $[M(solv)_x]^+[B(OTeF_5)_4]^-$. In the case of Ag^+ and 1,1,2-trichlorotrifluoroethane, the unsolvated compound $AgB(OTeF_5)_4$ was isolated as crystals belonging to the monoclinic system ($P2_1/n$, $a = 11.419$ (7) Å, $b = 10.329$ (4) Å, $c = 15.31$ (1) Å, $\beta = 91.53$ (5)°, $Z = 4$, $T = -127$ °C). The Ag^+ ion is bonded weakly to three $B(OTeF_5)_4^-$ ions, with three Ag–O contacts (2.500 (5)–2.756 (5) Å) and six Ag–F interactions (2.644 (5)–3.017 (5) Å). In the case of Tl^+ and either dichloromethane or 1,1,2-trichlorotrifluoroethane, the unsolvated salt $TlB(OTeF_5)_4$ is formed. Both $AgB(OTeF_5)_4$ and $TlB(OTeF_5)_4$ are thermally unstable, slowly forming $MOTeF_5$ and volatile $B(OTeF_5)_3$. This decomposition is slower for Tl^+ (days) than for Ag^+ (hours). Oxygen-17 NMR experiments demonstrate that the $OTeF_5^-$ substituents in $B(OTeF_5)_4^-$ do not exchange rapidly with free $OTeF_5^-$ but are rapidly exchanged in the presence of Lewis acids such as H^+, Ag^+, and $B(OTeF_5)_3$. Reactions of $AgB(OTeF_5)_4$ or $TlB(OTeF_5)_4$ with Fe(Por)Cl (Por = tetraphenylporphyrinate dianion or octaethylporphyrinate dianion) or Ph_3SiCl in dichloromethane or mesitylene produce $B(OTeF_5)_3$ and $Fe(Por)OTeF_5$ or $Ph_3SiOTeF_5$, respectively—the putative unsaturated cations $Fe(Por)^+$ or Ph_3Si^+ were not observed. In the case of Ph_3SiCl, the unsaturated cation Ph_3Si^+ or some similar species may be an intermediate, since Ph_3SiCl does not react directly with $N(n\text{-}Bu)_4B(OTeF_5)_4$. The reaction of $Ph_3CB(OTeF_5)_4$ with Ph_3SiH in dichloromethane also produces $Ph_3SiOTeF_5$.

Introduction

It has been nearly 20 years since Rosenthal published his brief review titled "The Myth of the Non-Coordinating Anion".[1] With the advent of modern techniques for eliminating water from reaction mixtures[2] and of automated X-ray diffraction equipment, the classical "noncoordinating" anions ClO_4^-,[3] $CF_3SO_3^-$,[4] FSO_3^-,[4] BF_4^-,[5] PF_6^-,[6] SbF_6^-,[7] and BPh_4^-[8] have been shown to coordinate

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to metal ions from all regions of the periodic table. It is not so important that the terms "noncoordinating anion" and "noncoordinating solvent" be expunged from the chemical literature as it is for chemists to recognize that they are relative terms. What is probably nonexistent is a *persistent* vacant coordination site—in a condensed phase, even the most weakly basic anions or the most weakly basic solvents will fill a truly vacant site.

In 1986 Reed and co-workers dubbed the carborane anion $B_{11}CH_{12}^-$ the "least coordinating" anion.[9] The virtues of this species, which was first prepared by Knoth in 1967,[10] are that its single negative charge is dispersed over a large number of atoms and that it does not contain any lone pairs or π electrons (as does, for example, BPh_4^- and its derivatives). In a series of elegant studies, Reed and co-workers showed that this icosahedral anion, despite its diffuse charge, formed M–H(B) bonds, where M is either Ag[11] or Fe.[9,12] Nevertheless, the complex $Fe(TPP)B_{11}CH_{12}$ has the weakest iron–anion interaction of any five-coordinate ferric porphyrin, as judged by the very small out-of-plane displacement of the Fe atom from the mean porphyrin plane (0.10 Å) as well as by magnetic criteria.[9,12b,13]

Another candidate for the least coordinating anion was reported by this laboratory in 1987.[14] The $B(OTeF_5)_4^-$ anion, first prepared by Sladky in 1980,[15] was used to isolate the $Tl(mes)_2^+$ cation, which contains two η^6-mesitylene ligands.[14,16] As with $B_{11}CH_{12}^-$, the $B(OTeF_5)_4^-$ anion is not noncoordinating—the structure of $Tl(mes)_2B(OTeF_5)_4$ revealed four weak Tl–F(Te) contacts (3.17 (1)–3.83 (2) Å). We have also reported the structure of $Tl(1,2\text{-}C_2H_4Cl_2)B(OTeF_5)_4$, in which the chlorocarbon molecule is coordinated, in bidentate fashion, to the Tl^+ ion.[17] This compound contains nine Tl–F(Te) contacts (2.950 (5)–3.981 (8) Å). More recently, we reported the synthesis and structure of $Ag(CO)B(OTeF_5)_4$, the first example of an isolable silver carbonyl.[18] The interactions between the cation and the anion are even stronger in this compound: the $Ag(CO)^+$ cation is linked to the $B(OTeF_5)_4^-$ anion by two Ag–O(Te) bonds (2.324 (6) and 2.436 (7) Å) and four weaker Ag–F(Te) bonds (2.969 (6)–3.076 (8) Å).

The isolation of a truly four-coordinate $Fe(Por)^+$ cation is only one of two acid tests for "noncoordinating" anions. The other synthetic goal, which has received far more attention over the years, is R_3Si^+, the silicenium (or silylenium) ion. Controversy surrounds recent reports of the generation of Ph_3Si^+ in the presence of ClO_4^- in dichloromethane or sulfolane solution.[19] There is no controversy, however, about the nature of Ph_3SiClO_4 in the solid state—it is a perchloryl ester with a moderately strong Si–O(Cl) bond (1.744 (4) Å).[19e]

By their nature, weakly coordinating anions will tend to be very large molecular ions with the potential of dissociating into smaller, more strongly coordinating fragments. In this paper, we report on the stability of the $B(OTeF_5)_4^-$ anion, especially with respect to transfer of an $OTeF_5^-$ (teflate) fragment to electrophilic centers such as H^+, Ag^+, Tl^+, BCl_3, $B(OTeF_5)_3$, $Fe(Por)^+$, and Ph_3Si^+. We also report the synthesis and structure of $AgB(OTeF_5)_4$. The spectroscopic and structural studies reported herein provide some clues about the conditions under which the $B(OTeF_5)_4^-$ anion might decompose into $OTeF_5^-$ and $B(OTeF_5)_3$ and, more importantly, provide a basis for designing larger but more stable counterions.

Experimental Section

Air-Sensitivity, Solvents, and Starting Materials. Virtually all of the compounds used in this study were sensitive to traces of moisture. All manipulations were performed under vacuum or under a purified dinitrogen atmosphere using standard techniques.[2a,b] Dichloromethane, dichloromethane-d_2, 1,2-dichloroethane, 1,2-dichloroethane-d_4, and 1,1,2-trichlorotrifluoroethane were distilled from P_2O_5, toluene and mesitylene (mes) were distilled from sodium, and acetonitrile-d_3 was distilled from calcium hydride. Boron trichloride (Matheson CP) was vacuum distilled prior to use. The compounds Ph_3CCl, Ph_3SiCl, and Ph_3SiH (Aldrich) were recrystallized from dichloromethane. The compounds $HOTeF_5$,[20,21] $N(n\text{-}Bu)_4OTeF_5$,[20] $N(n\text{-}Bu)_4H(OTeF_5)_2$,[20] $B(OTeF_5)_3$,[15,21] $AgOTeF_5$,[22] $TlOTeF_5$,[14] $Tl(mes)_2B(OTeF_5)_4$,[14] $Fe(TPP)Cl$,[13,23] and $Fe(OEP)Cl$[13,23] were prepared by literature procedures. The compound $N(n\text{-}Bu)_4B(OTeF_5)_4$[14] was prepared by a literature procedure and was recrystallized from dichloromethane. The isotopically labeled compound $H^{17}OTeF_5$ was prepared using the published procedure for $H^{18}OTeF_5$,[24] substituting $H_2{}^{17}O$ for $H_2{}^{18}O$.

Spectroscopic Measurements. Samples for IR spectroscopy were Nujol mulls between KBr or AgCl windows. Spectra were recorded at room temperature on a Perkin-Elmer 983 spectrometer. Peak positions are ±1 cm^{-1}. Samples for NMR spectroscopy were dichloromethane solutions in 5- or 10-mm glass tubes. Spectra were recorded, after shimming the magnet with a separate sample of neat dichloromethane-d_2, at room temperature on a Bruker SY-200 or WP-300 spectrometer, operating at the indicated frequencies: ^{11}B (64.2 MHz on SY-200); ^{13}C (50.3 MHz on SY-200); ^{17}O (40.7 MHz on WP-300); ^{19}F (188.3 MHz on SY-200, 282.4 MHz on WP-300). Chemical shifts (δ scale) are relative to Et_2OBF_3 using 10% v/v BCl_3 in dichloromethane as a secondary external standard (δ 47.0) for ^{11}B, internal Me_4Si for ^{13}C, external neat H_2O for ^{17}O, and internal $CFCl_3$ for ^{19}F. All ^{19}F NMR spectra of $OTeF_5$ compounds were AB_4X patterns shielded relative to $CFCl_3$ ($X = {}^{125}Te$, $I = {}^1/_2$, 7% natural abundance). Fluorine-19 chemical shifts and J_{AB} values were determined by comparing experimental spectra to simulated spectra that were calculated using LAOCOON PC.[25] Values of J_{AX}

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Table I. Details of the X-ray Diffraction Study of $AgB(OTeF_5)_4$

compd	$AgB(OTeF_5)_4$
molecular formula	$AgBF_{20}O_4Te_4$
fw	1073.0
space group	$P2_1/n$
unit cell dimens	
a, Å	11.419 (7)
b, Å	10.329 (4)
c, Å	15.306 (10)
β, deg	91.53 (5)
V, Å^3	1805 (1)
Z	4
calcd density, g cm^{-3}	3.95
cryst dimens, mm	0.20 × 0.28 × 0.68
data collcn temp, °C	−125 (1)
radiation (λ, Å)	Mo Kα (0.7107)
monochromator	graphite
abs coeff, cm^{-1}	79
scan type	θ–2θ
scan speed, deg min^{-1}	variable (4–30)
2θ range, deg	4–55
reflcns	$h,k,\pm l$
tot. no. of reflcns measd	4579
no. of obsd reflcns, $\lvert F \rvert > 2.5\sigma(F_o)$	3858
data/param ratio	14.24
R	0.045
R_w	0.067
GOF	1.764
g (refined)	9.4×10^{-4}
slope of normal probability plot	1.423

and J_{BX} were measured, when possible, directly from the experimental spectra.

$Ph_3SiOTeF_5$. The compounds Ph_3SiCl (1.02 g, 3.46 mmol) and $TlOTeF_5$ (1.47 g, 3.33 mmol) were dissolved in toluene, and the solution was stirred for 12 h (a slight excess of Ph_3SiCl was used to aid in the purification of the product). After filtration of TlCl and removal of toluene under vacuum, the white solid product was recrystallized from dichloromethane. Yield: 0.90 g (54%). ^{19}F NMR (CH_2Cl_2): δ_A −39.2, δ_B −40.9, J_{AB} = 190 Hz, J_{BX} = 3560 Hz. ^{13}C NMR (CH_2Cl_2): δ_{ortho} 128.9, δ_{meta} 135.8, δ_{para} 132.0, δ_{ipso} 131.5 (cf. Ph_3SiCl, δ_{ortho} 128.5, δ_{meta} 131.2, δ_{para} 135.5, δ_{ipso} 133.2).

$Ph_3CB(OTeF_5)_4$. The compounds Ph_3CCl (0.40 g, 1.4 mmol) and $Tl(mes)_2B(OTeF_5)_4$ (2.0 g, 1.4 mmol) were dissolved in dichloromethane. A white precipitate of TlCl formed immediately. The reaction mixture was filtered after stirring for 30 min, leaving a clear, very dark orange filtrate. Cooling the filtrate to −78 °C produced dark orange crystals. Yield: 1.0 g (60%). Further concentration of the supernatant produced an additional 20–25% of crystalline product. ^{19}F NMR (CH_2Cl_2): δ_A −38.8, δ_B −45.9, J_{AB} = 182 Hz, J_{AX} = 3330 Hz, J_{BX} = 3560 Hz. ^{13}C NMR (CH_2Cl_2): δ_{ortho} 142.9, δ_{meta} 131.0, δ_{para} 143.9, δ_{ipso} 140.3 (cf. Ph_3CClO_4,[19d] δ_{ortho} 143.2, δ_{meta} 131.0, δ_{para} 143.8, δ_{ipso} 140.4).

$AgB(OTeF_5)_4$ and $Ag(1,2\text{-}C_2H_4Cl_2)_2B(OTeF_5)_4$. The compounds $AgOTeF_5$ (0.52 g, 1.5 mmol) and $B(OTeF_5)_3$ (1.1 g, 1.5 mmol) were dissolved in 1,2-dichloroethane (10 mL). The colorless solution was kept in the freezer (−20 °C) for 24 h, at which time the crystalline compound $Ag(1,2\text{-}C_2H_4Cl_2)_2B(OTeF_5)_4$ was present (stoichiometry determined by NMR spectroscopy (see below)). Like $Tl(1,2\text{-}C_2H_4Cl_2)B(OTeF_5)_4$,[17] this compound also slowly loses the coordinated 1,2-dichloroethane molecules under a dinitrogen atmosphere. Therefore, the % yield cannot be determined and elemental analysis was not attempted. The unsolvated compound $AgB(OTeF_5)_4$ was prepared by mixing $AgOTeF_5$ (0.26 g, 0.76 mmol) and $B(OTeF_5)_3$ (0.54 g, 0.74 mmol) in 1,1,2-trichlorotrifluoroethane (2 mL). All of the borane dissolved, but much solid, white $AgOTeF_5$ was present. The mixture was kept in the freezer (−20 °C) for 24 h, at which time colorless crystals of $AgB(OTeF_5)_4$ were present. The crystals were separated from excess, undissolved $AgOTeF_5$ with a spatula. The unsolvated compound $AgB(OTeF_5)_4$ is thermally unstable: within hours a significant portion has decomposed to form $AgOTeF_5$ and $B(OTeF_5)_3$. ^{19}F NMR of $AgB(OTeF_5)_4$ (CH_2Cl_2): δ_A −38.9, δ_B −46.0, J_{AB} = 187 Hz, J_{AX} = 3320 Hz, J_{BX} = 3570 Hz.

X-ray Crystallographic Study of $AgB(OTeF_5)_4$. A Nicolet R3m diffractometer equipped with a LT-1 variable-temperature accessory was used. Crystals of $AgB(OTeF_5)_4$ were examined under argon at approximately −180 °C. A suitable crystal was attached with Dow-Corning silicone grease to the end of a glass fiber and quickly placed into the cold nitrogen stream of the LT-1 unit.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $AgB(OTeF_5)_4$

atom	x	y	z	U_{iso}[a]
Ag	−2602 (1)	721 (1)	8177 (1)	32 (1)
B	−2292 (7)	2074 (8)	6321 (5)	23 (2)
O1	−1457 (4)	1898 (6)	7056 (3)	28 (2)
O2	−3414 (4)	1773 (5)	6741 (4)	27 (2)
O3	−2272 (4)	3384 (5)	5963 (3)	21 (1)
O4	−2070 (5)	1172 (5)	5621 (3)	28 (2)
Te1	13 (1)	2593 (1)	7287 (1)	22 (1)
Te2	−4888 (1)	2490 (1)	6675 (1)	25 (1)
Te3	−2104 (1)	3999 (1)	4832 (1)	22 (1)
Te4	−2174 (1)	−599 (1)	5553 (1)	26 (1)
F1	−572 (5)	4263 (5)	7260 (4)	38 (2)
F2	368 (4)	2756 (5)	6136 (3)	34 (1)
F3	696 (4)	1002 (5)	7331 (4)	39 (2)
F4	−308 (5)	2455 (6)	8446 (3)	44 (2)
F5	1422 (4)	3294 (5)	7587 (3)	40 (2)
F6	−4314 (5)	4161 (5)	6834 (4)	44 (2)
F7	−4970 (5)	2293 (6)	7853 (3)	46 (2)
F8	−5556 (4)	897 (5)	6513 (4)	37 (2)
F9	−4851 (5)	2727 (5)	5491 (3)	37 (2)
F10	−6349 (5)	3175 (7)	6660 (5)	61 (2)
F11	−1156 (4)	5246 (5)	5325 (3)	35 (2)
F12	−3343 (4)	5076 (5)	5016 (3)	37 (2)
F13	−3071 (5)	2816 (5)	4301 (3)	39 (2)
F14	−836 (4)	3019 (5)	4588 (3)	33 (1)
F15	−1929 (5)	4792 (6)	3776 (3)	47 (2)
F16	−2341 (4)	−821 (5)	6746 (3)	34 (1)
F17	−3765 (5)	−583 (6)	5411 (4)	45 (2)
F18	−2003 (5)	−566 (5)	4373 (3)	45 (2)
F19	−596 (5)	−792 (6)	5713 (4)	53 (2)
F20	−2266 (6)	−2372 (5)	5507 (4)	56 (2)

[a] The equivalent isotropic U is defined as one-third of the trace of the $\mathbf{U}_{ij}$ tensor.

Centering on 25 reflections allowed least-squares calculation[26] of the cell constants, which are listed, along with other experimental values, in Table I. The intensities of control reflections 200, 020, and 002, monitored every 97 reflections, showed no significant trend during the course of the data collection. An empirical absorption correction, based on intensity profiles for 16 reflections over a range of setting angles (ψ) for the diffraction vector, were applied to the observed data. The transmission factors ranged from 0.125 to 0.206. Lorentz and polarization corrections were applied to the data.

The structure was solved using direct methods.[26] Final refinements involved anisotropic thermal parameters for all atoms. Neutral-atom scattering factors (including anomalous scattering) were taken from ref 27. The weighted least-squares refinements converged (weights calculated as $(\sigma^2(F) + \lvert gF_o^2 \rvert^{-1})$, with the average shift/esd <0.005 over the last three refinement cycles. In the final difference Fourier maps, the maximum and minimum electron densities were 2.03 (0.84 Å from Te2) and −1.58 e Å^{-3}. Analysis of variance as a function of Bragg angle, magnitude of F_o, reflection indices, etc. showed no significant trends. Final atomic positional parameters and isotropic thermal parameters are listed in Table II.

Results and Discussion

Synthesis, Spectral Properties, and Structure of $B(OTeF_5)_4^-$. Since the first teflate compound, $HOTeF_5$, was reported by Engelbrecht and Sladky in 1964,[28] chemists have recognized the electronic similarity between the $OTeF_5$ substituent and a fluorine atom (i.e., hard and *very* electronegative).[29] Coupled with the fact that teflate is essentially inert to loss of a fluoride ion or a fluorine atom,[30] it seemed logical to explore the $B(OTeF_5)_4^-$ anion

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(26) Calculations for diffractometer operations were performed by using software supplied with the Nicolet R3m diffractometer. All structural calculations were performed on the Data General Eclipse S/140 computer in the X-ray laboratory at Colorado State University with the SHELXTL program library written by Professor G. M. Sheldrick and supplied by Siemens Analytical X-Ray Corp.

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Table III. Spectroscopic Results for Salts of $B(OTeF_5)_4^{-}$[a]

cation	δ_A[b]	J_{AX},[c] Hz	ν(TeO),[d] cm^{-1}
Ph_3C^+	−38.8	3330	797 (w), 719 (s), 705 (sh)
Ag^+	−38.9	3320	787 (w), 723 (s, bd)
$Ag(CO)^+$[e]			774 (w, sh), 726 (s)
$Ag(1,2\text{-}C_2H_4Cl_2)_2^+$			797 (w), 721 (s, bd)
Tl^+[f]	−38.5	*g*	799 (w), 723 (s), 706 (s)
$Tl(1,2\text{-}C_2H_4Cl_2)^+$[f]			798 (w), 721 (s), 705 (s)
$Tl(mesitylene)_2^+$[h]	−38.2	3330	797 (w), 715 (s, bd)
$N(n\text{-}Bu)_4^+$[h]	−38.8	3330	797 (w), 712 (s, bd)

[a] All data from this work unless otherwise noted. [b] Fluorine-19 chemical shift of the F atom trans to O; solvent is dichloromethane. [c] One-bond coupling constant between Te and the F atom trans to O; solvent is dichloromethane. [d] From solid-state (Nujol mull) IR spectra; w = weak, s = strong, bd = broad, and sh = shoulder. [e] Data from ref 18; this compound is unstable in dichloromethane solution. [f] Data from ref 17. [g] Did not observe. [h] Data from ref 14.

as a very bulky and less coordinating alternative to BF_4^-. However, instead of using BF_4^- salts as starting materials, all examples of $B(OTeF_5)_4^-$ salts have been prepared by mixing $B(OTeF_5)_3$ with various $M^+OTeF_5^-$ compounds (M^+ = Cs^+,[15] Tl^+,[14] $N(n\text{-}Bu)_4^+$,[14] Ag^+[18]).

The NMR and IR spectral properties of $Tl(mes)_2B(OTeF_5)_4$ and $N(n\text{-}Bu)_4B(OTeF_5)_4$ have been discussed at length and compared with other teflate compounds in an earlier paper.[14] Here we will review only some essential features. Fluorine-19 NMR spectroscopy is routinely used for the study of teflate compounds.[31] The strength of the bond between the teflate oxygen atom and the element to which it is attached has a significant effect on the chemical shift of the fluorine atom trans to the oxygen atom (δ_A) and on the coupling constant between this fluorine atom and its tellurium atom (J_{AX}).[20,24,31] The parameters δ_A and J_{AX} (dichloromethane solution) vary from −19.0 ppm and 2660 Hz for $N(n\text{-}Bu)_4OTeF_5$ to −46.2 ppm and 3650 Hz for $B(OTeF_5)_3$. When these two compounds are combined to make $N(n\text{-}Bu)_4B(OTeF_5)_4$, the NMR parameters change to the intermediate values −38.3 ppm and 3330 Hz. This illustrates the diagnostic value of ^{19}F NMR spectra for this class of compounds. Nevertheless, there are only very minor changes in these two parameters for various salts of our borate anion, as shown in Table III. Therefore, ^{19}F NMR spectroscopy, while helpful for verifying the purity of the compounds in this study, was not useful for distinguishing the degree of coordination and/or ion pairing of the $B(OTeF_5)_4^-$ anion to different cations.

The TeO stretching frequency is also sensitive to the environment of the teflate oxygen atom.[20,24,32] The highest value is found for the free $OTeF_5^-$ anion in salts such as $N(n\text{-}Bu)_4OTeF_5$ (867 cm^{-1}).[20] In the $B(OTeF_5)_4^-$ anion, the Te–O bonds are longer than in free teflate, and the TeO stretching frequencies are correspondingly lower, as shown in Table III (compare Te–O bond distances of 1.807 (8)–1.827 (9) Å in $Tl(1,2\text{-}C_2H_4Cl_2)B(OTeF_5)_4$[17] with the Te–O bond distance in the free $OTeF_5^-$ anion,[24] 1.786 (3) Å). The bands at ~797 cm^{-1} (weak) and ~720 cm^{-1} (strong) are assigned as the "A_1" and "T_2" stretching normal modes for the four TeO oscillators in the $B(OTeF_5)_4^-$ anion. The symmetric stretch at ~797 cm^{-1} is IR active (albeit weak) because the $B(OTeF_5)_4^-$ anion does not possess strict T_d symmetry (see below). For a few of the cations, splitting of the T_2 mode is apparent; in most cases, however, the splitting is unresolved. In summary, the NMR and IR data in Table III clearly illustrate that the interactions of the $B(OTeF_5)_4^-$ anion with various counterions are sufficiently weak that spectroscopic criteria proving coordination have not yet been, and may not ever be, established for this large polyfluorinated anion.

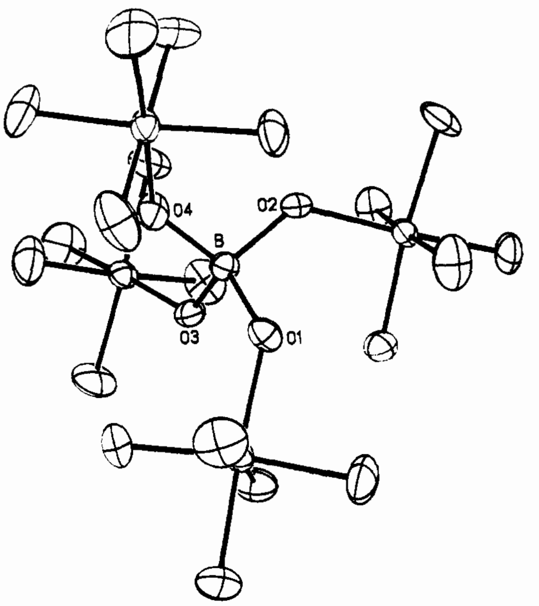

Figure 1. $B(OTeF_5)_4^-$ anion in $Tl(1,2\text{-}C_2H_4Cl_2)B(OTeF_5)_4$ (50% probability ellipsoids). To facilitate the discussion, the oxygen atom numbering scheme is different from that in ref 17 (O1, O2, O3, and O4 in this figure correspond to O3, O1, O2, and O4 in ref 17).

The structure of the $B(OTeF_5)_4^-$ anion in $Tl(1,2\text{-}C_2H_4Cl_2)B(OTeF_5)_4$[17] is shown in Figure 1. The four teflate groups fit together without any obvious distortions from normal (i.e., "octahedral") teflate geometry;[24] the B–O–Te angles, which range from 128.3 (7) to 133.4 (7)°, are not essentially different from the 132.3 (4)° angle in $B(OTeF_5)_3$.[33] In the sterically more congested compounds $U(OTeF_5)_6$[34] and $Te(OTeF_5)_6$,[35] the M–O–Te bond angles are ~170 and ~139°, respectively. For the $B(OTeF_5)_4^-$ anion in the related compound $Tl(mes)_2B(OTeF_5)_4$,[14] the closest F⋯F distance between teflate groups is 2.87 (2) Å, while F⋯F distances within each teflate group are ~2.5–2.6 Å.

Four different Tl^+ ions make weak contacts (2.950 (5)–3.981 (8) Å) with nine F atoms of the $B(OTeF_5)_4^-$ anion in $Tl(1,2\text{-}C_2H_4Cl_2)B(OTeF_5)_4$, but the bonds between Te atoms and F atoms coordinated to Tl^+ ions are not significantly longer than the other Te–F distances in this compound (generally, coordination of an anion such as SbF_6^- produces a longer Sb–F bond distance to the bridging F atom,[7b] but this is not always the case[7a]). The anion has idealized S_4 symmetry, the highest symmetry possible if the F atoms are ignored (cf. $B(OH)_4^-$, for which the highest possible symmetry is also S_4). Rigorous S_4 symmetry would require that each Te–O vector be parallel to a B–O vector belonging to a second oxygen atom and that its projection onto the O–B–O plane for the remaining oxygen atoms bisects the O–B–O angle. The data for the Te2–O2 vector shown in Figure 1 (i.e., the Te–O vector involving O2) are representative and show that the correspondence to S_4 symmetry is only approximate: the Te2–O2–B–O4 torsional angle, which ideally should be 180°, is 167.5°, while the Te2–O2–B–O3 and Te2–O2–B–O1 torsional angles, which ideally should be equal in magnitude, are −72.9 and 46.5°, respectively. The Te4–O4 vector, however, is nearly ideally oriented—in this case, the three relevant angles are 179.8, −57.9, and 59.2°.

Structure of $AgB(OTeF_5)_4$. A drawing of the asymmetric unit of this compound is shown in Figure 2, along with the numbering scheme used. The Ag(I) ion coordination sphere, emphasizing the bonds to oxygen atoms, is shown in Figure 3. Selected bond distances and angles are listed in Table IV. Complete lists of bond distances and angles, anisotropic thermal parameters, and

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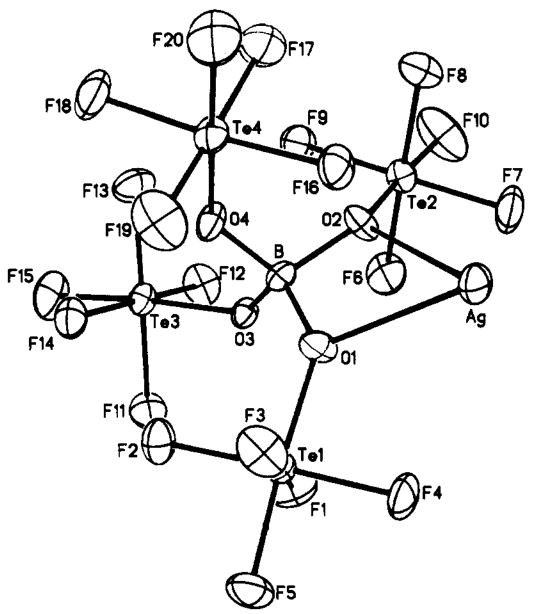

Figure 2. Asymmetric unit of $AgB(OTeF_5)_4$ (50% probability ellipsoids).

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) for $AgB(OTeF_5)_4$

Ag–O1	2.500 (5)	Ag–O2	2.601 (5)
Ag–O3′	2.756 (5)	Ag–F16	2.730 (5)
Ag–F1′	2.644 (5)	Ag–F6′	2.717 (6)
Ag–F11′	2.773 (5)	Ag–F12′	3.017 (5)
Ag–F20″	2.824 (6)	B–O1	1.466 (9)
B–O2	1.48 (1)	B–O3	1.46 (1)
B–O4	1.45 (1)	Te–O	1.836 (5)–1.858 (5)
Te–F	1.812 (5)–1.860 (5)		
O1–Ag–O2	53.0 (2)	O1–Ag–O3′	142.1 (2)
O2–Ag–O3′	138.4 (2)	O1–Ag–F11′	160.4 (2)
O2–Ag–F12′	167.9 (2)	F16–Ag–F20″	171.0 (2)
Ag–O1–Te1	123.1 (2)	Ag–O2–Te2	121.3 (3)
Ag–O3′–Te3′	98.8 (2)	Ag–O1–B	104.2 (4)
Ag–O2–B	99.3 (4)	Ag–O3′–B′	129.1 (4)
O1–B–O2	101.1 (5)	O–B–O[a]	108.3 (6)–112.8 (6)
B–O–Te	131.7 (5)–133.8 (5)	O–Te–F_{ax}	173.3 (2)–178.8 (3)
O–Te–F_{eq}	86.1 (2)–96.3 (2)		

[a] This is the range for the five O–B–O angles other than O1–B–O2.

observed and calculated structure factors are available as supplementary material, as is a stereoview showing the unit cell packing.

From the standpoint of assessing the coordinating ability of the borate anion, the most important feature of the structure is that borate–cation bridging involves the teflate oxygen atoms, unlike the situation in $Tl(1,2\text{-}C_2H_4Cl_2)B(OTeF_5)_4$ and $Tl(mes)_2B(OTeF_5)_4$. The Ag^+ ion is bonded to O1 (2.500 (5) Å) and O2 (2.601 (5) Å) from one borate anion and more weakly bonded to O3′ (2.756 (5) Å) from another. To put these Ag–O(Te,B) distances in perspective, they can be compared with Ag–O(Te,M) distances in $[Ag(toluene)_2OTeF_5]_2$ (2.368 (3), 2.396 (3) Å),[22] $[Ag(1,2\text{-}C_2H_4Cl_2)OTeF_5]_2$ (2.308 (7)–2.362 (7) Å),[36] $[Ag(1,2,3\text{-}C_3H_5Cl_3)OTeF_5]_2$ (2.376 (4), 2.468 (4) Å)[37] (M = Ag), $Ag_2(CH_2Cl_2)_4Pd(OTeF_5)_4$ (2.404 (5), 2.532 (4) Å),[36] and $Ag_2(1,2\text{-}C_2H_4Cl_2)_4Pd(OTeF_5)_4$ (2.372 (3), 2.777 (2) Å) (M = Pd).[36] The Ag–O(Te,B) distances in $AgB(OTeF_5)_4$ can also be compared with the Ag–O(Te,B) distances recently found in $Ag(CO)B(OTeF_5)_4$,[18] which are 2.324 (6) and 2.436 (7) Å.

Differences in ionic radii may explain why Ag^+ coordinates to $B(OTeF_5)_4^-$ oxygen atoms and Tl^+ does not. According to Shannon's compilation, the six-coordinate radii of Ag^+ and Tl^+ are 1.15 and 1.50 Å, respectively.[38] Clearly, the oxygen atoms are sterically less accessible than the fluorine atoms, and the larger Tl^+ ion may not be able to form Tl–O(Te,B) bonds without requiring a severe distortion of the borate anion. An alternative explanation may be that the Ag^+ ions in the two compounds in question either have no ancillary ligands or only a sterically innocent one (i.e., CO): perhaps with a set of larger ligands, as in the compound $Ag(1,2\text{-}C_2H_4Cl_2)_2B(OTeF_5)_4$, Ag–O(Te,B) bonds would be absent.

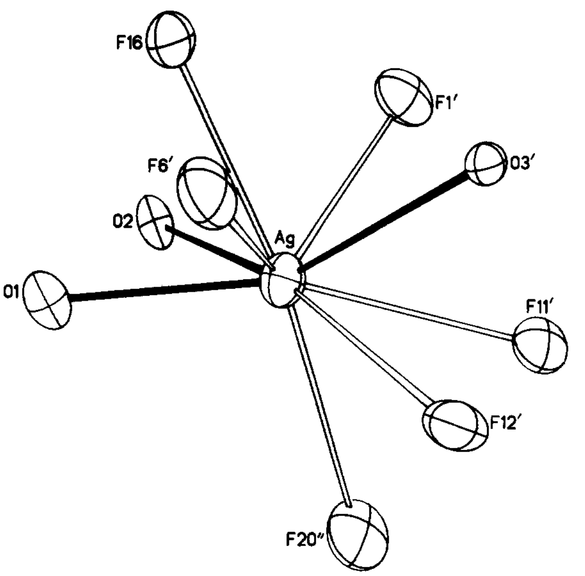

Figure 3. Coordination sphere of the Ag^+ ion in $AgB(OTeF_5)_4$ (50% probability ellipsoids).

Six fluorine atoms round out the coordination sphere of the Ag^+ ion in $AgB(OTeF_5)_4$, one from the anion that provides O1 and O2, four from the anion that provides O3′, and one from another borate anion (see Figure 3). The Ag–F(Te) bonds range in distance from 2.644 (5) Å for F1′ to 3.017 (5) Å for F12′. These are comparable with the Ag–F(Te) bonds found in the above-mentioned structures: $[Ag(1,2\text{-}C_2H_4Cl_2)OTeF_5]_2$ (2.772 (6)–2.990 (7) Å, $[Ag(1,2,3\text{-}C_3H_5Cl_3)OTeF_5]_2$ (2.986 (4), 3.178 (3) Å), $Ag_2(CH_2Cl_2)_4Pd(OTeF_5)_4$ (3.030 (4) Å), and $Ag(CO)B(OTeF_5)_4$ (2.959 (6)–3.076 (8) Å). The Ag–F distances in $AgSbF_6$[39] and AgF,[40] both of which have AgF_6 coordination spheres, are 2.62 and 2.467 (3) Å, respectively. As has been found in the three other structures containing the $B(OTeF_5)_4^-$ anion, the Te–F(Ag) bonds in $AgB(OTeF_5)_4$ are not statistically longer than the other Te–F bonds in this compound.

The structures of the borate anions shown in Figures 1 and 2 differ in a subtle but significant way. The teflate group containing O2 in $AgB(OTeF_5)_4$ has rotated by 92.3° about the B–O2 vector relative to its position in $Tl(1,2\text{-}C_2H_4Cl_2)B(OTeF_5)_4$. This distortion from S_4 symmetry, which leaves the borate anion in $AgB(OTeF_5)_4$ with no idealized element of symmetry, is necessary for it to function as an O,O′-bidentate ligand. This can be appreciated by considering that the O1, O2, and O3 atoms in $AgB(OTeF_5)_4$ each have a nearly planar configuration (i.e., the sum of the three angles around each of these atoms is 359.0 (7), 354.4 (7), and 359.9 (6)°, respectively. Note that the near-planarity of three-coordinate teflate oxygen atoms is a common feature of teflate structural chemistry.[22,36,37] The third "coordination sites" for the O1 and O2 atoms in the borate anion in $Tl(1,2\text{-}C_2H_4Cl_2)B(OTeF_5)_4$ are not aimed at a common point, whereas upon rotation of the O2 teflate group both O1 and O2 can simultaneously have a planar configuration and coordinate to the Ag^+ ion.

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An issue that will be addressed in the following section of this paper is transfer of an intact teflate anion from $B(OTeF_5)_4^-$ to an electrophilic center, such as Ag^+. One might expect that Ag–O(Te,B) bridging should weaken the corresponding B–O bonds. This does occur in the compound $Ag(CO)B(OTeF_5)_4$—the B–O(Te,Ag) bond distances (both are 1.50 (1) Å) are longer than the B–O(Te) bond distances (both are 1.44 (1) Å).[18] For $AgB(OTeF_5)_4$, however, the B–O bonds involving O1, O2, and O3 are not longer, within experimental error, than B–O4.

The only other distortion of the $B(OTeF_5)_4^-$ anion in $AgB(OTeF_5)_4$ relative to the anion in $Tl(mes)_2B(OTeF_5)_4$ or $Tl(1,2\text{-}C_2H_4Cl_2)B(OTeF_5)_4$ is the closing of the O–B–O angle for the oxygen atoms involved in the four-membered $\overline{\text{Ag–O–B–O}}$ chelate ring (this angle is 101.1 (5)°, whereas the other five range from 108.3 (6) to 112.8 (6)°). The chelate ring is relatively planar (the maximum deviation from the least-squares plane is 0.12 Å for B) and exhibits a small bite angle (i.e., the O–Ag–O angle is 53.0 (2)°). Both the planarity and small bite angle are common features of four-membered chelate rings such as those formed by carboxylates[41] and dithiocarbamates.[42]

Stability of $B(OTeF_5)_4^-$ in the Presence of Electrophiles. (a) Stability in the Solid State. The formation of $B(OTeF_5)_4^-$ from $B(OTeF_5)_3$ and salts of $OTeF_5^-$ can be thought of as an equilibrium that is highly solvent dependent (i.e., ligand dependent) in many cases, even in the solid state:

$$M^+OTeF_5^- + B(OTeF_5)_3 \rightleftharpoons M^+B(OTeF_5)_4^-$$

For example, when M^+ is Cs^+,[15] Ph_3C^+, or $N(n\text{-}Bu)_4^+$, the solid borate salt is stable indefinitely, even under vacuum (note that $B(OTeF_5)_3$ is quite volatile and can be easily sublimed at room temperature[21]). Whatever solvent is used serves only as a vehicle for mixing the reagents together. When M^+ is Ag^+ or Tl^+, however, the equilibrium lies to the left unless ligands are present. The stability of the Cs^+ salt relative to the Ag^+ and Tl^+ salts may be due to the larger radius of Cs^+ (1.67 Å for six-coordination vs 1.15 and 1.50 Å for Ag^+ and Tl^+, respectively[38]).

The greater stability of large, complex anions in the presence of large cations, a classic principle of inorganic chemistry,[43] is apparently at work here. The thermodynamic terms that are involved are the enthalpy of the bond broken by fragmentation of the complex anion and the difference in lattice enthalpies for the complex anion salt and the fragment salt. The enthalpy of $OTeF_5^-$ dissociation from $B(OTeF_5)_4^-$ is not known, but the lattice enthalpies of $AgOTeF_5$ and $AgB(OTeF_5)_4$ may be estimated as follows. Bartlett and co-workers recently described the following remarkably simple empirical relationship, which allows the lattice enthalpy for an A^+X^- salt to be estimated knowing only its formula unit volume (the units for U and V are kcal mol^{-1} and $Å^3$, respectively):[44]

$$U = 556.3(V^{-1/3}) + 26.3$$

This relationship works well for the alkali-metal halides and for the few BF_4^- salts that have had their lattice enthalpies determined. Some error might be expected for silver salts since covalency may be present, but since we are dealing with fluoroanions, the error is probably small. (In fact, the lattice enthalpy of AgF is 231 kcal mol^{-1},[45] while the value calculated using the formula unit volume of AgF[40] is 227 kcal mol^{-1}.) The formula unit volume of $AgOTeF_5$ is unknown, but it is probably very close to that of $AgSbF_6$ (120 $Å^3$),[39] since the unit cell parameters of $CsOTeF_5$[32b] and $CsSbF_6$[46] are the same to within experimental error. The formula unit volume of $AgB(OTeF_5)_4$ is 452 $Å^3$ (see Table I). Therefore, the empirically derived lattice enthalpies of $AgOTeF_5$ and $AgB(OTeF_5)_4$ are 139 and 99 kcal mol^{-1}, and ΔU = 40 kcal mol^{-1}. This means that the enthalpy for $OTeF_5^-$ dissociation from $B(OTeF_5)_4^-$ must be less than 40 kcal mol^{-1}. Furthermore, the difference in lattice enthalpies is undoubtedly the reason that $AgB(OTeF_5)_4$ is soluble in 1,1,2-trichlorotrifluoroethane while $AgOTeF_5$ is not (see below).

The ligands that stabilize $AgB(OTeF_5)_4$ and $TlB(OTeF_5)_4$ in the solid state can be CO[18] or solvent molecules such as arene hydrocarbons and chlorocarbons. For these weakly coordinating solvents, solutions of $M(solv)_x^+B(OTeF_5)_4^-$ are formed. Saturated solutions of $AgB(OTeF_5)_4$ and $TlB(OTeF_5)_4$ in 1,1,2-trichlorotrifluoroethane, the weakest donor solvent we have worked with to date, are 4 and 0.8 mM, respectively. We suggest that the dissolved metal ions are complexed by solvent via M–Cl(C) bonds, forming $Ag(1,1,2\text{-}C_2Cl_3F_3)_x^+$ and $Tl(1,1,2\text{-}C_2Cl_3F_3)_x^+$ ions. This type of weak bonding has been confirmed by X-ray crystallography for Ag^+ and Tl^+ with the more strongly coordinating solvents dichloromethane, 1,2-dichloroethane, and 1,2,3-trichloropropane.[17,36,37] The coordination of the chlorofluorocarbon molecules cannot yet be proven, since upon crystallization only the solvent-free salts $AgB(OTeF_5)_4$ and $TlB(OTeF_5)_4$ are obtained. Even using the more coordinating solvent dichloromethane, only unsolvated $TlB(OTeF_5)_4$ is obtained upon crystallization. Using 1,2-dichloroethane, however, affords the crystalline compounds $Ag(1,2\text{-}C_2H_4Cl_2)_2B(OTeF_5)_4$ and $Tl(1,2\text{-}C_2H_4Cl_2)B(OTeF_5)_4$. The stoichiometry of the thallium compound was proven by crystallography, while the stoichiometry of the silver compound was proven by dissolving a weighed sample of it in acetonitrile-d_3 and comparing the integral of the methylene proton resonance with a standard.

As crystals form in a solution of $M(solv)_x^+B(OTeF_5)_4^-$, metal–solvent bonds may be broken in order to produce a smaller cation (this would lead to a higher lattice enthalpy). In essence, the coordinated solvent molecules are "squeezed" out of the lattice if the metal–solvent bonds are not strong enough. It is sensible that 1,2-dichloroethane, which forms five-membered chelate rings, is a stronger ligand than dichloromethane, which can only form more strained four-membered chelate rings. This trend was recently demonstrated for $M^+ = Ag^+$ by structural, conductimetric, and ^{13}C NMR data.[22] Solubility data for $TlOTeF_5$ lead to the same conclusion: 1,2-dichloroethane, 30.2 mM; dichloromethane, 1.1 mM (note that 1,2-dichloroethane and dichloromethane have similar dielectric constants, 10.65 and 9.08, respectively[47]). Consistent with our assumption that chlorofluorocarbons are weaker donors that chlorocarbons, $TlOTeF_5$ is completely insoluble in 1,1,2-trichlorotrifluoroethane.[48]

(b) Stability in Solution. Since one of our primary reasons for studying the $B(OTeF_5)_4^-$ anion was to generate and characterize reactive cationic species such as $Fe(Por)^+$ and Ph_3Si^+, one of our primary concerns had to be the propensity of this complex anion to fragment *in solution* into $OTeF_5^-$ and $B(OTeF_5)_3$. Despite the substantial Lewis acidity of $B(OTeF_5)_3$ (the enthalpy of formation of its adduct with pyridine is more negative than that of BF_3 and approximately equal to that of BCl_3[30]), "naked" cationic metal and metalloid centers can be expected to be even more acidic as well as highly electrophilic, and equilibria such as

$$Fe(Por)^+ + B(OTeF_5)_4^- \rightleftharpoons Fe(Por)OTeF_5 + B(OTeF_5)_3$$

might lie far to the right. Therefore, the rate at which $B(OTeF_5)_4^-$ undergoes unimolecular or bimolecular teflate transfer may be the key to its usefulness or limitation. We noted above that

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Table V. ^{17}O and ^{11}B NMR Results[a]

compd	$\delta(^{17}O)$[b,c]	$\delta(^{11}B)$[b,d]	exch with $N(n\text{-}Bu)_4B(OTeF_5)_4$[e]
$N(n\text{-}Bu)_4B(OTeF_5)_4$	119	14.5 (13.9[f])	
$B(OTeF_5)_3$	120 (121.5[g,h])	1.1 (0.7[i])	+[j]
BCl_3		47.0	−
$N(n\text{-}Bu)_4OTeF_5$	180 (178.5[g,k])		−
$N(n\text{-}Bu)_4H(OTeF_5)_2$	135		−
$HOTeF_5$	100 (93.7[g,h])		+
$AgOTeF_5$	109		+

[a] All data from this work unless otherwise noted; concentrations ca. 0.1 M in dichloromethane at 22 °C. [b] Literature values in parentheses. [c] Relative to H_2O. [d] Relative to Et_2OBF_3. [e] A + sign implies that exchange of teflate groups is complete within 1 h at 22 °C; a − sign implies that no exchange is detectable after 1 h. [f] Reference 15; solvent is acetonitrile. [g] Schrobilgen, G. J. Unpublished data, 1991. [h] Solvent is sulfonyl chloride fluoride (SO_2ClF). [i] Reference 15; solvent is 1,1,2-trichlorotrifluoroethane. [j] This exchange reaction was monitored by IR spectroscopy and was complete after 24 h (see text). [k] Solvent is acetonitrile.

$AgB(OTeF_5)_4$ and $TlB(OTeF_5)_4$, while stable indefinitely in solution, decompose in the solid state to $MOTeF_5$ and $B(OTeF_5)_3$. The rates were not the same: the silver salt, with its bridge bonds between the Ag^+ ion and the borate's oxygen atoms, decomposed within hours, while the thallium salt decomposed over several days. Steric factors, including access to oxygen atoms, may also control the rate of decomposition in solution.

We prepared a number of ^{17}O-labeled teflate compounds in order to monitor the exchange of teflate groups with $B(OTeF_5)_4^-$ in dichloromethane. Representative ^{17}O NMR spectra are shown in Figure 4, and relevant data are listed in Table V. The first experiment performed was to mix together $N(n\text{-}Bu)_4{}^{17}OTeF_5$ and $N(n\text{-}Bu)_4B(OTeF_5)_4$. Even after many days, no exchange of teflate anions was observed (i.e., the intensity of the ^{17}O NMR resonance at 180 ppm was unchanged, and no peak was observed at 119 ppm). This proves that fragmentation of the borate anion into a teflate anion and $B(OTeF_5)_3$ is not a rapid process at 22 °C. If transfer of a teflate group is found to occur, it must be promoted by an electrophilic center.

The uncharged, molecular electrophiles BCl_3 and $B(OTeF_5)_3$ were tested next. Boron-11 NMR spectroscopy was used for the BCl_3 experiment (see Table V). After 24 h, a 2:1 mole ratio mixture of BCl_3 and $N(n\text{-}Bu)_4B(OTeF_5)_4$ showed no signs of ligand exchange; i.e., only two ^{11}B NMR resonances at 47.0 and 1.1 ppm were observed. After 45 days, five resonances were observed at 47.0, 30.9, 11.2, 4.0, and 1.1 ppm, suggesting that chloride/teflate metathesis is occurring but only very slowly. Alternatively, adventitious water leaking into the sample over the long period of time could lead to species such as HCl or $HOTeF_5$, either of which could promote the exchange reaction.

Neither ^{11}B nor ^{17}O NMR spectroscopy could be easily used to monitor a mixture of $N(n\text{-}Bu)_4B(OTeF_5)_4$ and $B(OTeF_5)_3$. The high cost of isotopically pure ^{10}B compounds was one factor. The other was that the ^{17}O resonances for these two compounds are nearly the same, and since they are broad (due to the quadrupolar nature of ^{17}O), it would not be possible to observe one resonance grow in at the expense of the other. Instead, equimolar amounts of $N(n\text{-}Bu)_4B(OTeF_5)_4$ and $B(^{18}OTeF_5)_3$ (~90% isotopic enrichment) were mixed in 1,2-dichloroethane at 22 °C for 24 h. After removal from the reaction mixture and purification by vacuum distillation,[21] the borane was treated with excess concentrated sulfuric acid:

$$B(OTeF_5)_3 \xrightarrow{H_2SO_4} 3HOTeF_5 + B(HSO_4)_3$$

The teflic acid produced, purified by vacuum distillation,[20] was treated with excess pyridine, and the IR spectrum of the resulting $pyHOTeF_5$ was recorded. Comparison of the intensities of the peaks due to $\nu(Te^{16}O)$ and $\nu(Te^{18}O)$ at 851 and 806 cm^{-1}, respectively, revealed that the ^{18}O label was nearly completely scrambled. It is not clear why BCl_3 does not rapidly abstract a teflate group from $B(OTeF_5)_4^-$ while the sterically more encumbered Lewis acid $B(OTeF_5)_3$ does.

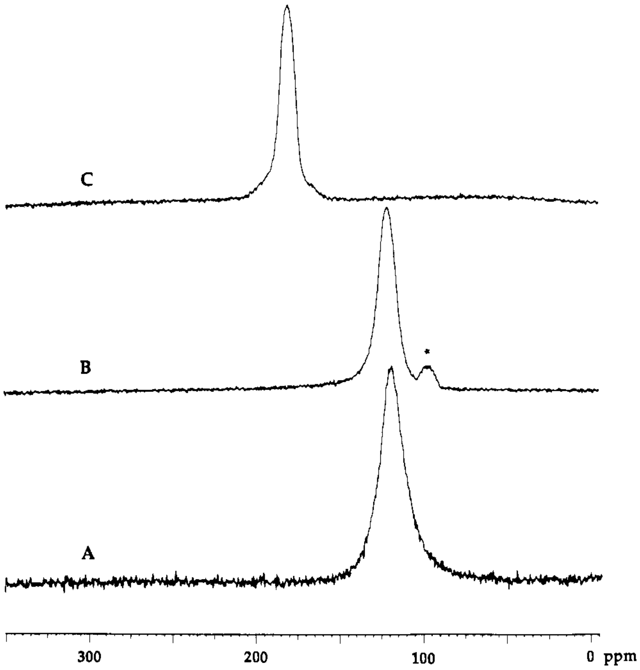

Figure 4. 40.7-MHz ^{17}O NMR spectra of $N(n\text{-}Bu)_4B(OTeF_5)_4$ (A), $B(OTeF_5)_3$ (B), and $N(n\text{-}Bu)_4OTeF_5$ (C) in dichloromethane solution at 22 °C. The peak marked with an asterisk in spectrum B is due to $HOTeF_5$.

The exchange reactions of $N(n\text{-}Bu)_4B(OTeF_5)_4$ and either $H^{17}OTeF_5$ or $Ag^{17}OTeF_5$ were complete within 1 h. Both H^+ and Ag^+ can form bridge bonds to borate oxygen atoms, and apparently this leads to rapid exchange in solution. The structures of $AgB(OTeF_5)_4$ and $Ag(CO)B(OTeF_5)_4$ prove the existence of bridge bonds for Ag^+, while the structure of $N(n\text{-}Bu)_4H(OTeF_5)_2$,[20] which contains a strong O–H–O hydrogen bond, provides a model for the proposed $[F_5TeO{-}H{-}O(TeF_5){-}B(OTeF_5)_3^-]$ intermediate. Interestingly, the salt $N(n\text{-}Bu)_4H(^{17}OTeF_5)_2$ does not undergo rapid teflate exchange with $N(n\text{-}Bu)_4B(OTeF_5)_4$, presumably because the proton is already strongly bonded to two oxygen atoms. In summary, rapid fragmentation of the $B(OTeF_5)_4^-$ anion requires the presence of electrophiles, either neutral ($B(OTeF_5)_3$) or cationic (H^+ or Ag^+).

Attempts To Generate $Fe(Por)^+$ and Ph_3Si^+. Iron porphyrins are one of the most studied and best characterized classes of transition-metal complexes.[49] Of the six different combinations of oxidation state (II and III) and ligation state (four-, five-, and six-coordinate), only four-coordinate, planar Fe(III) has not yet been prepared or generated in solution.[50] The complex that is closest in spectroscopic and magnetic properties to those anticipated for $Fe(Por)^+$ is $Fe(TPP)(B_{11}CH_{12})$,[9,12b] which exhibits a Fe–H(B) distance of 1.82 (4) Å and a displacement of the Fe atom from the mean porphyrin plane of 0.10 Å (cf. $Fe(TPP)SbF_6$, 0.15 Å,[51] $Fe(TPP)ClO_4$, 0.30 Å,[52] and Fe(TPP)I, 0.53 Å[53]).

We attempted to generate $Fe(TPP)^+$ and $Fe(OEP)^+$ in mesitylene solution by reaction of Fe(TPP)Cl or Fe(OEP)Cl with either $AgB(OTeF_5)_4$ or $TlB(OTeF_5)_4$. All reaction mixtures gave similar results: a very slow metathesis reaction ensued (i.e., slow precipitation of AgCl or TlCl). However, there was no evidence for

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Fe(Por)$^+$ or for the B(OTeF$_5$)$_4^-$ anion after the reaction was complete. Instead, examination of the products by IR spectroscopy revealed that Fe(TPP)OTeF$_5$ (ν(TeO) = 849 cm^{-1}[54]) or Fe(OEP)OTeF$_5$ (ν(TeO) = 852 cm^{-1}[54]) had formed. If four-coordinate Fe(TPP)$^+$ or Fe(OEP)$^+$ cations had formed during the reactions, they quickly abstracted a teflate ligand from the borate anion. Even though the porphyrin cations (especially Fe(TPP)$^+$) possess some element of steric hindrance, it is conceivable that intermediates such as [(TPP)Fe–O(TeF$_5$)–B(OTeF$_5$)$_3$] are involved in these reactions.

There have been many attempts to generate and study three-coordinate silicon cations (silicenium or silylenium ions). A review of the work published prior to 1974 was written by Corriu and Henner.[55] More recent summaries are also available.[19] Despite the apparent stability of R$_3$Si$^+$ species in the gas phase,[56] no unequivocal evidence for their persistent existence in a condensed phase has been published. Recent claims[19c,d] that compounds such as Ph$_3$SiClO$_4$ and Me$_3$SiClO$_4$ are extensively ionized in dichloromethane or sulfolane have been questioned by others.[19a,b,e]

The method used by Lambert and co-workers to generate Ph$_3$SiClO$_4$ and other trisubstituted silyl perchlorates was pioneered by Corey[57] and is shown in the following equation:

$$R_3SiH + Ph_3CClO_4 \rightarrow R_3SiClO_4 + Ph_3CH$$

This reaction relies on the greater strength of C–H vs Si–H bonds.[58] Since we anticipated that the B(OTeF$_5$)$_4^-$ ion would be less coordinating than perchlorate, we attempted to generate the Ph$_3$Si$^+$ ion by mixing together dichloromethane solutions of Ph$_3$SiH and Ph$_3$CB(OTeF$_5$)$_4$. After 30 min, the reaction mixture was examined by ^{13}C and ^{19}F NMR spectroscopy, which showed the presence of Ph$_3$SiOTeF$_5$ and B(OTeF$_5$)$_3$. No evidence for a cationic silicon center was observed.

An alternative means of generating Ph$_3$Si$^+$ was also investigated. The reaction of Tl(mes)$_2$B(OTeF$_5$)$_4^-$ with Ph$_3$SiCl in mesitylene solution yielded the expected white TlCl precipitate after several hours (gravimetric analysis revealed that the reaction was not complete at this point). After filtration, only Ph$_3$SiCl and Ph$_3$SiOTeF$_5$ could be observed by NMR spectroscopy. For both reactions, presumably, an electrophilic species that could be three-coordinate Ph$_3$Si$^+$ is formed and rapidly abstracts a teflate group from the borate anion. Control experiments showed that neither Ph$_3$SiH nor Ph$_3$SiCl reacted with N(n-Bu)$_4$B(OTeF$_5$)$_4$—the presence of an electrophile, whose role is to remove H$^-$ or Cl$^-$, is required for the formation of Ph$_3$SiOTeF$_5$.

Summary and Conclusions. Despite the large size and diffuse charge of the B(OTeF$_5$)$_4^-$ anion, its usefulness as a weakly coordinating anion is limited for two reasons. First, it is not large enough to cause lattice energies of its Ag$^+$ and Tl$^+$ salts to be small enough to allow very weak donor solvents such as chlorofluorocarbons to remain coordinated to the metal ions in the solid state. Second, it too easily fragments into OTeF$_5^-$ and B(OTeF$_5$)$_3$ in the presence of strong electrophiles (the teflate anion is a moderately strong anionic ligand—its coordinating ability lies between that of Cl$^-$ and ClO$_4^-$[22,54,59]). What is needed is an even larger anion, and if it is to be based on OTeF$_5^-$ substituents, the oxygen atoms will have to be sterically less accessible to electrophiles. Possibilities include Nb(OTeF$_5$)$_6^-$,[60] Ta(OTeF$_5$)$_6^-$,[60] and Sb(OTeF$_5$)$_6^-$.[61] A good structural model for the latter anion is the isoelectronic compound Te(OTeF$_5$)$_6$.[35] With six teflate groups around a central atom and Te–O–Te bond angles around 139°, the oxygen atoms appear to be well shielded from attack by external electrophiles. The use of these three extremely large octahedral species as weakly coordinating anions is currently being explored in this laboratory.

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Registry No. Ph$_3$SiOTeF$_5$, 139494-61-4; Ph$_3$CB(OTeF$_5$)$_4$, 139494-62-5; AgB(OTeF$_5$)$_4$, 135480-98-7; Ag(1,2-C$_2$H$_4$Cl$_2$)$_2$B(OTeF$_5$)$_4$, 139494-63-6; Ph$_3$SiCl, 76-86-8; TlOTeF$_5$, 104528-77-0; Tl(mes)$_2$B(OTeF$_5$)$_4$, 139494-64-7; AgOTeF$_5$, 50700-88-4; B(OTeF$_5$)$_3$, 40934-88-1; TlB(OTeF$_5$)$_4$, 139494-65-8; Fe(TPP)OTeF$_5$, 113704-01-1; Fe(OEP)OTeF$_5$, 113704-02-2; Fe(TPP)Cl, 16456-81-8; Fe(OEP)Cl, 28755-93-3; Ph$_3$SiH, 789-25-3; N(n-Bu)$_4$B(OTeF$_5$)$_4$, 108711-77-9; HOTeF$_5$, 57458-27-2.

Supplementary Material Available: A stereoview showing crystal packing and complete tables of bond distances, bond angles, and anisotropic thermal parameters for AgB(OTeF$_5$)$_4$ (6 pages); a table of observed and calculated structure factors for AgB(OTeF$_5$)$_4$ (25 pages). Ordering information is given on any current masthead page.

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