

and may reflect a kinetic effect in the synthetic process.

The  $pK_a$  for the deprotonation is 3.78 ( $\pm 0.02$ ) in aqueous solution ( $\mu = 0.1$ ; 25.0 °C). By comparison, the  $pK_a$  of coordinated 2-pyridinemethanol in the complex  $[\text{Ru}(\text{bpy})_2((\text{py})\text{CH}_2\text{OH})]^{2+}$  is 7.2 ( $\pm 0.1$ ) under the same conditions;<sup>36</sup> the higher acidity of coordinated tris(2-pyridyl)methanol probably reflects additional steric strain within the tripodal ligand. There is no evidence for protonation of the free py N atom in the N,N',O-coordinated ligand even at pH ca. 1. The  $pK_a$  values of the free ligand  $(\text{py})_3\text{COH}$  in 95% methanol are 4.9 ( $\pm 0.1$ ) and 1.9 ( $\pm 0.1$ ), with the third value probably slightly lower than 1.5;<sup>12</sup> while the  $pK_a$  of the alcohol OH is significantly lowered by coordination to the positive metal center, the nonprotonation of the free py N is clearly unusual, since the  $pK_a$  values of the uncoordinated py N atoms in a number of polypyridyl-type ligands are actually raised by their coordination in a monodentate manner to Ru(II).<sup>35,37</sup> In the present case, one possibility is that in solution the coordinated -OH is hydrogen-bonded to the py N in the free ring, thereby forming a five-membered ring (-O(1)-H(1)...N(3)-C(32)-C(2)-, in the numbering scheme used in Figure 3) and inhibiting protonation of N(3). This is not the case for the solid state, however, where Figure 3 reveals that the free pyridine ring is rotated so that the nitrogen atom (N(3)) points away from the O(1)-H(1), and the -OH group is in fact hydrogen bonded to an oxygen atom of a methyl sulfate anion (Table S11).

The deprotonation is also associated with a color change of the complex from yellow to orange (see Table VI and Figure 1) and a cathodic shift in the redox potential of the Ru(III)/Ru(II) couple from 0.40 to 0.25 V. A reduction in redox potential is generally observed on lowering of the overall complex charge.<sup>38</sup> The po-

tential of the Ru(III)/Ru(II) couple for the nondeprotonated species **2**,  $E_{1/2} = 0.40$  V, compares with 0.62 V for  $[\text{Ru}(\text{bpy})_2((\text{py})\text{CH}_2\text{OH})]^{3+/2+}$ <sup>36</sup> under the same conditions.

Studies of the photochemical properties of the ruthenium(II) complexes of a variety of tripodal  $\pi$ -acceptor ligands will be published subsequently, but preliminary measurements with the deprotonated complex **1** indicate a luminescence lifetime of ca. 1.4 ns.<sup>39</sup>

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**Registry No.** **1a**, 108451-82-7; **2a**, 108451-84-9;  $[\text{Ru}((\text{py})_3\text{COH})((\text{py})_3\text{CO})]\text{BF}_4$ , 108451-80-5;  $[\text{Ru}((\text{py})_3\text{COH})((\text{py})_3\text{CO})]\text{Br}$ , 108451-81-6;  $[\text{Ru}(\text{H})(\text{OH})_2(\text{CH}_3\text{OH})(\text{PPh}_3)_2]\text{BF}_4$ , 60020-13-5; tris(2-pyridyl)methanol, 73569-80-9.

**Supplementary Material Available:** Tables listing positional and isotropic thermal parameters for the refined hydrogen atoms in **2** (Table S1), anisotropic thermal parameters for the non-hydrogen atoms in **1** (Table S2) and **2** (Table S3), atomic coordinates for the hydrogen atoms in **1** (Table S4) and **2** (Table S5), bond distances and angles for **1** (Table S6) and **2** (Table S7), hydrogen bonding in **1** (Table S10) and **2** (Table S11), and best planes for **1** (Table S12) and **2** (Table S13) (19 pages); tables of observed and calculated structure factors for **1** (Table S8) and **2** (Table S9) (37 pages). Ordering information is given on any current masthead page.

(36) Ridd, M. J.; Keene, F. R.; Gakowski, D. J.; Sneddon, G. E., manuscript in preparation.

(37) Lavalley, D. K.; Fleischer, E. B. *J. Am. Chem. Soc.* **1972**, *94*, 2583-2599.

(38) Ridd, M. J.; Keene, F. R. *J. Am. Chem. Soc.* **1981**, *103*, 5733-5740 and references quoted therein.

(39) Winkler, J. R.; Keene, F. R., unpublished work.

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## A New Candidate for the Least Coordinating Anion: Preparation and Characterization of $[\text{TlOTeF}_5(\text{mes})_2]_2 \cdot \text{mes}$ (mes = Mesitylene) and $[\text{Tl}(\text{mes})_2^+][\text{B}(\text{OTeF}_5)_4^-]$

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The compounds  $\text{TlOTeF}_5$ ,  $[\text{TlOTeF}_5(\text{mes})_2]_2 \cdot \text{mes}$  (mes = mesitylene), and  $[\text{Tl}(\text{mes})_2^+][\text{B}(\text{OTeF}_5)_4^-]$  have been prepared and characterized by <sup>19</sup>F NMR and vibrational spectroscopy. In addition, the structures of the last two compounds have been determined by X-ray diffraction. The compound  $[\text{TlOTeF}_5(\text{mes})_2]_2 \cdot \text{mes}$  crystallizes in the triclinic space group  $P\bar{1}$ . Unit cell parameters are  $a = 11.048$  (3) Å,  $b = 14.643$  (3) Å,  $c = 16.345$  (4) Å,  $\alpha = 102.43$  (2)°,  $\beta = 99.10$  (2)°,  $\gamma = 92.70$  (2)°, and  $Z = 2$ . The nearly centrosymmetric  $[\text{TlOTeF}_5(\text{mes})_2]_2$  dimer contains a nearly planar  $\text{Tl}_2\text{O}_2$  core, with two  $\text{OTeF}_5$  groups bridging the two thallium atoms. The mesitylene ligands are  $\eta^6$ -coordinated to the thallium atoms and make dihedral angles of 51.5 and 49.0° within each of the independent  $[\text{Tl}(\text{mes})_2^+]$  moieties. The compound  $[\text{Tl}(\text{mes})_2^+][\text{B}(\text{OTeF}_5)_4^-]$  crystallizes in the orthorhombic system, space group  $Pbc2_1$ . Unit cell parameters are  $a = 10.659$  (3) Å,  $b = 16.383$  (8) Å,  $c = 20.165$  (6) Å, and  $Z = 4$ . The structure consists of a chain of  $[\text{Tl}(\text{mes})_2^+]$  cations and  $[\text{B}(\text{OTeF}_5)_4^-]$  anions connected by extremely weak  $\text{Tl} \cdots \text{F}$  interactions. The  $\text{Tl}-\text{C}$  distances within the  $[\text{Tl}(\text{mes})_2^+]$  cations of  $[\text{Tl}(\text{mes})_2^+][\text{B}(\text{OTeF}_5)_4^-]$  are substantially shorter than in  $[\text{TlOTeF}_5(\text{mes})_2]_2 \cdot \text{mes}$ . In all other respects, the  $[\text{Tl}(\text{mes})_2^+]$  moieties in these two compounds are structurally very similar. The  $[\text{B}(\text{OTeF}_5)_4^-]$  anion is extremely weakly coordinated to  $\text{Tl}(\text{I})$  in this salt, with four  $\text{Tl} \cdots \text{F}$  contacts that range from 3.17 to 3.83 Å.

### Introduction

We have been investigating the chemistry of the teflate<sup>1</sup> anion ( $\text{OTeF}_5^-$ ) with respect to its use as a ligand for coordination and organometallic compounds. Complexes such as  $\text{Mn}(\text{CO})_5(\text{OTeF}_5)$ ,<sup>2</sup>  $[\text{AgOTeF}_5(\text{tol})_2]_2$  (tol = toluene),<sup>3</sup>  $\text{Fe}(\text{OTeF}_5)_3$ ,<sup>4</sup> and  $\text{Pt}$ -

$(\text{OTeF}_5)_2(\text{nor})$  (nor = norbornadiene)<sup>5</sup> reveal that the electronic and structural properties of teflate are quite different from those of any other anionic ligand including  $\text{ClO}_4^-$  and  $\text{CF}_3\text{SO}_3^-$ . We have also been exploring the use of  $[\text{B}(\text{OTeF}_5)_4^-]$  as a potentially noncoordinating anion with which coordinatively unsaturated metal and non-metal cations could be isolated. Since the charge should

(1) Abbreviations: teflate = pentafluoroorthotellurate; teflic acid = pentafluoroorthotelluric acid; TPP = 5,10,15,20-tetraphenylporphyrinate dianion.

(2) Strauss, S. H.; Abney, K. D.; Long, K. M.; Anderson, O. P. *Inorg. Chem.* **1984**, *23*, 1994.

(3) Strauss, S. H.; Noirot, M. D.; Anderson, O. P. *Inorg. Chem.* **1985**, *24*, 4307.

(4) Strauss, S. H.; Miller, P. K., unpublished data, 1985.

(5) Colman, M. R.; Manning, M. C.; Anderson, O. P.; Strauss, S. H., submitted for publication.

be localized primarily on the boron and oxygen atoms, the fluorine atoms on the periphery of this anion should be much weaker donors than the fluorine atoms of BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, etc. or the oxygen atoms of ClO<sub>4</sub><sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, etc. Each member of this list of nominally "noncoordinating" anions has been found to coordinate to metal ions in many cases.<sup>6</sup>

We originally prepared AgOTeF<sub>5</sub>·CH<sub>2</sub>Cl<sub>2</sub><sup>3</sup> and [AgOTeF<sub>5</sub>(tol)<sub>2</sub>]<sub>2</sub><sup>3</sup> as halide/teflate metathesis reagents, so that a wide variety of metal halide complexes could be converted to the corresponding metal teflate complexes. For example, Fe(TPP)Cl<sup>1</sup> reacts cleanly with AgOTeF<sub>5</sub>·CH<sub>2</sub>Cl<sub>2</sub> to produce Fe(TPP)(OTeF<sub>5</sub>).<sup>7</sup> However, since Ag(I) oxidizes some low-valent metal ions (e.g. Rh(I)), an alternate metathesis reagent was sought. We eventually prepared the stoichiometrically simple compound TlOTeF<sub>5</sub>, and as has been the case in our previous studies of metal teflate complexes, we discovered several unusual and unexpected things about its chemistry. Most notable is its high solubility in aromatic hydrocarbons. This behavior, while not unprecedented for Tl(I) salts,<sup>8</sup> is rare.

In this paper we report our findings on the synthesis and characterization of TlOTeF<sub>5</sub>, [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub>·mes (mes = mesitylene), and [Tl(mes)<sub>2</sub>]<sup>+</sup>[B(OTeF<sub>5</sub>)<sub>4</sub>]<sup>-</sup>, including a determination of the structure of the last two compounds by X-ray diffraction. A preliminary report of the structure of [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub> has been reported.<sup>9</sup> There is only one other example of a structurally characterized Tl(I)-arene complex.<sup>8b</sup> Moreover, the structure of [Tl(mes)<sub>2</sub>]<sup>+</sup>[B(OTeF<sub>5</sub>)<sub>4</sub>]<sup>-</sup> demonstrates that the B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> anion is extremely weakly coordinated to Tl(I) in this salt. While there may be no such thing as a "noncoordinating" anion in condensed media, the B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> anion is an excellent candidate for the least coordinating anion.<sup>6b</sup>

## Experimental Section

**Reagents and Solvents.** Benzene, benzene-*d*<sub>6</sub>, toluene, mesitylene, and hexane were distilled from sodium. Dichloromethane and dichloromethane-*d*<sub>2</sub> were distilled from calcium hydride. These solvents were stored under vacuum or under a purified dinitrogen atmosphere prior to use. Thallium(I) fluoride (Cerac) was used as received. Teflic acid<sup>1</sup> (HOTeF<sub>5</sub>),<sup>10</sup> B(OTeF<sub>5</sub>)<sub>3</sub>,<sup>11</sup> and [N(*n*-Bu)<sub>4</sub>]<sup>+</sup>[OTeF<sub>5</sub>]<sup>-</sup><sup>10</sup> were prepared as previously described.

In the following preparations and physical measurements, all operations were carried out with rigorous exclusion of dioxygen and water. Schlenk, glovebox, and high-vacuum techniques were employed, with purified dinitrogen used when an inert atmosphere was required.

**Physical Measurements.** Samples for <sup>19</sup>F NMR spectroscopy were dichloromethane, toluene, or mesitylene solutions with 1% CFC<sub>3</sub> added. Chemical shifts (δ scale) are relative to the CFC<sub>3</sub> internal standard.

**Table I.** Experimental Parameters for the X-ray Diffraction Studies

mol formula	[TlOTeF <sub>5</sub> (mes) <sub>2</sub> ] <sub>2</sub> ·mes	[Tl(mes) <sub>2</sub> ] <sup>+</sup> - [B(OTeF <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>
mol wt	1486.9	1410.0
space group	<i>P</i> $\bar{1}$	<i>Pbc</i> 2 <sub>1</sub> <sup>a</sup>
unit cell dimens		
<i>a</i> , Å	11.048 (3)	10.659 (3)
<i>b</i> , Å	14.643 (3)	16.383 (8)
<i>c</i> , Å	16.345 (4)	20.165 (6)
α, deg	102.43 (2)	90
β, deg	99.10 (2)	90
γ, deg	92.70 (2)	90
unit cell vol, Å <sup>3</sup>	2540.6 (7)	3521 (2)
Z	2	4
caled density, g cm <sup>-3</sup>	1.94	2.66
cryst dimens, mm	0.170 (100 → $\bar{1}00$ ) × 0.090 (001 → 00 $\bar{1}$ ) × 0.070 (010 → 0 $\bar{1}0$ ) × 0.095 (011 → 0 $\bar{1}1$ )	0.040 (010 → 0 $\bar{1}0$ ) × 0.220 (100 → $\bar{1}00$ ) × 0.201 (10 $\bar{1}$ → $\bar{1}0\bar{1}$ ) × 0.183 (001 → 00 $\bar{1}$ )
data collec temp, <sup>b</sup> °C	-130 (1)	-130 (1)
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
monochromator	graphite	graphite
abs coeff, cm <sup>-1</sup>	76.1	81.09
2θ range, deg	4-50	4-50
reflens	± <i>h</i> , ± <i>k</i> , - <i>l</i>	<i>hkl</i>
no. of reflens	6486 ( <i>F</i> <sub>o</sub> > 2.5σ( <i>F</i> <sub>o</sub> ))	2736 ( <i>F</i> <sub>o</sub> > 4σ( <i>F</i> <sub>o</sub> ))
total no. of reflens measd	8945	3492
scan type	ω, Wyckoff	θ-2θ
scan speed (deg min <sup>-1</sup> )	variable (6-30)	variable (2-30)
data/param ratio	10.9	6.9
<i>R</i>	0.054	0.043
<i>R</i> <sub>w</sub>	0.044	0.046
GOF	1.16	1.16
<i>g</i>	4.0 × 10 <sup>-3</sup> (fixed)	1.6 × 10 <sup>-3</sup> (refined)
slope of normal probability plot	1.02	1.004

<sup>a</sup>A variant of *Pca*2<sub>1</sub>, No. 29. <sup>b</sup>Obtained with a Nicolet LT-1 accessory.

Spectra were recorded at room temperature on a Bruker SY-200 spectrometer operating at 188.31 MHz. All <sup>19</sup>F NMR spectra were AB<sub>4</sub>X patterns upfield of CFC<sub>3</sub> (X = <sup>125</sup>Te, 7.0% natural abundance, *I* = 1/2). Samples for <sup>1</sup>H NMR spectroscopy were benzene-*d*<sub>6</sub> solutions. Spectra were recorded at room temperature on a Bruker SY-270 spectrometer operating at 270.13 MHz. Samples for IR spectroscopy were mulls (Nujol or Fluorolube, KBr windows) or solutions (dichloromethane or toluene, 0.2 mm path length IR-tran cells). Spectra were recorded on a Perkin-Elmer 983 spectrometer calibrated with polystyrene. Band positions are ±1 cm<sup>-1</sup>. Samples for Raman spectroscopy were crystalline or microcrystalline solids loaded into glass capillaries. Spectra were recorded with a Spex Ramalog 5 spectrophotometer calibrated with standard compounds. The 514.5-nm line of an argon ion laser was used to excite the samples. The apparent molecular weight of TlOTeF<sub>5</sub> in toluene was measured at 20.0 °C with use of an isopiestic molecular weight apparatus.<sup>12</sup> Tris(acetylacetonato)iron(III) (recrystallized from benzene) was used as the molecular weight standard.

**Preparation of Compounds.** TlOTeF<sub>5</sub>. Anhydrous TlF (13.0 g, 58.4 mmol) and toluene (50 mL) were charged into a stainless-steel vessel equipped with a stainless-steel valve and a Kel-F valve seat. Teflic acid (14.5 g, 60.5 mmol) was vacuum-transferred into the vessel at -196 °C. The reaction vessel was agitated for 7 days at room temperature, after which removal of all volatiles under vacuum left a free-flowing white powder. This was immediately dissolved in toluene (250 mL) and the mixture was filtered, leaving a colorless solution. Complete removal of toluene under vacuum at room temperature for several hours left 18.1 g of a white powder, formulated (see below) as TlOTeF<sub>5</sub> (70% based on TlF). <sup>19</sup>F NMR (toluene): δ<sub>A</sub> -24.0, δ<sub>B</sub> -33.1, *J*<sub>AB</sub> = 176 Hz, *J*<sub>AX</sub> = 3054 Hz, *J*<sub>BX</sub> = 3642 Hz.

[TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub>·mes. The white powdery compound TlOTeF<sub>5</sub> was dissolved in a minimum of mesitylene and the mixture was filtered, yielding a clear solution. Crystals suitable for diffraction were grown by slowly cooling this solution. These crystals rapidly lose mesitylene at room temperature under a dinitrogen atmosphere. The <sup>19</sup>F NMR

- (6) (a) Shelly, K.; Finster, D. C.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1985**, *107*, 5955. (b) Shelly, K.; Reed, C. A.; Lee, Y. J.; Scheidt, W. R. *J. Am. Chem. Soc.* **1986**, *108*, 3117. (c) Reed, C. A.; Mashiko, T.; Bentley, S. P.; Kastner, M. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948. (d) Shelly, K.; Bartczak, T.; Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1985**, *24*, 4325. (e) Hersh, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 4599. (f) Hitchcock, P. B.; Lappert, M. F.; Taylor, R. G. *J. Chem. Soc., Chem. Commun.* **1984**, 1082. (g) de Carvalho, L. C. A.; Dartiguenave, M.; Dartiguenave, Y.; Beauchamp, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 6848. (h) Humphrey, M. B.; Lamanna, W. M.; Brookhart, M.; Husk, G. R. *Inorg. Chem.* **1983**, *22*, 3355. (i) Buss, B.; Clegg, W.; Hartmann, G.; Jones, P. G.; Mews, R.; Noltemeyer, M.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1981**, 61. (j) Roberts, G. W.; Cummings, S. C.; Cunningham, J. A. *Inorg. Chem.* **1976**, *15*, 2503. (k) Rosenthal, M. R.; *J. Chem. Educ.* **1973**, *50*, 331. (l) Nolte, M. J.; Gafner, G.; Haines, L. M. *J. Chem. Soc., Chem. Commun.* **1969**, 1406. (m) Gowda, N. M. N.; Naikar, S. B.; Reddy, G. K. N. *Adv. Inorg. Chem. Radiochem.* **1984**, *28*, 255. (n) Johansson, L. *Coord. Chem. Rev.* **1974**, *12*, 241. (o) Lawrence, G. A. *Chem. Rev.* **1986**, *86*, 17. (p) Yared, Y. W.; Miles, S. L.; Bau, R.; Reed, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 7077.
- (7) Miller, P. K.; Pawlik, M. J.; Anderson, O. P.; Strauss, S. H., manuscript in preparation.
- (8) (a) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 893. (b) Schmidbaur, H.; Bublak, W.; Riede, J.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 414.
- (9) Strauss, S. H.; Noirot, M. D.; Anderson, O. P. *Inorg. Chem.* **1986**, *25*, 3850.
- (10) Strauss, S. H.; Abney, K. D.; Anderson, O. P. *Inorg. Chem.* **1986**, *25*, 2806.
- (11) Kropshofer, H.; Leitzke, O.; Peringer, P.; Sladky, F. *Chem. Ber.* **1981**, *114*, 2644.

- (12) Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969; p 73.

spectrum of  $\text{TiOTeF}_5$  in mesitylene ( $\delta_A -23.5$ ,  $\delta_B -33.2$ ,  $J_{AB} = 179$  Hz,  $J_{AX} = 3054$  Hz,  $J_{BX} = 3632$  Hz) is essentially the same as shown above for  $\text{TiOTeF}_5$  in toluene.

$[\text{Tl}(\text{mes})_2^+][\text{B}(\text{OTeF}_5)_4^-]$ . The compounds  $\text{TiOTeF}_5$  (1.30 g, 2.92 mmol) and  $\text{B}(\text{OTeF}_5)_3$  (2.12 g, 2.92 mmol) were mixed in mesitylene (20 mL). The white crystalline solid that formed was filtered out and washed with hexane. Yield: 3.35 g (89%). These crystals eventually lose mesitylene at room temperature under a dinitrogen atmosphere, but much more slowly than  $[\text{TiOTeF}_5(\text{mes})_2]_2\text{mes}$ .  $^{19}\text{F}$  NMR (dichloromethane, 76 mM):  $\delta_A -38.24$ ,  $\delta_B -45.40$ ,  $J_{AB} = 172$  Hz,  $J_{AX} = 3328$  Hz,  $J_{BX} = 3576$  Hz.  $^{19}\text{F}$  NMR (dichloromethane, 39 mM):  $\delta_A -38.33$ ,  $\delta_B -45.46$ ,  $J_{AB} = 172$  Hz,  $J_{AX} = 3328$  Hz,  $J_{BX} = 3576$  Hz.

$[\text{N}(\textit{n}\text{-Bu})_4^+][\text{B}(\text{OTeF}_5)_4^-]$ . Equivalent amounts of  $[\text{N}(\textit{n}\text{-Bu})_4^+][\text{OTeF}_5^-]$  and  $\text{B}(\text{OTeF}_5)_3$  were mixed in dichloromethane. All volatiles were removed under vacuum, leaving a white powder that was used without further purification.  $^{19}\text{F}$  NMR (dichloromethane, 75 mM):  $\delta_A -38.78$ ,  $\delta_B -45.93$ ,  $J_{AB} = 172$  Hz,  $J_{AX} = 3328$  Hz,  $J_{BX} = 3576$  Hz.  $^{19}\text{F}$  NMR (dichloromethane, 38 mM):  $\delta_A -38.84$ ,  $\delta_B -45.96$ ,  $J_{AB} = 172$  Hz,  $J_{AX} = 3328$  Hz,  $J_{BX} = 3576$  Hz.

**Crystallographic Study.** In both cases, colorless crystals of  $[\text{TiOTeF}_5(\text{mes})_2]_2\text{mes}$  and  $[\text{Tl}(\text{mes})_2^+][\text{B}(\text{OTeF}_5)_4^-]$  were centered on a Nicolet R3m diffractometer. Centering of 25 reflections allowed least-squares calculation<sup>13</sup> of the cell constants given in Table I. Other experimental parameters are also listed in Table I.

For the six-sided prismatic crystal of  $[\text{TiOTeF}_5(\text{mes})_2]_2\text{mes}$ , the intensities of control reflections ( $32\bar{1}$ ,  $34\bar{5}$ ,  $0\bar{3}\bar{5}$ ) monitored every 197 reflections showed no significant trend during the course of the data collection. An empirical absorption correction, based on intensity profiles of 17 reflections over a range of setting angles ( $\psi$ ) for the diffraction vector, was applied to the observed data. The applied transmission factors ranged from 0.562 to 0.409. Lorentz and polarization corrections were applied to the data.

The thallium and tellurium atoms were located by Patterson methods, and all other non-hydrogen atoms were located in difference Fourier maps, for which phases were determined by the previously located atoms. Subsequent refinement involved anisotropic thermal parameters for all non-hydrogen atoms. Neutral-atom scattering factors (including anomalous scattering) were taken from ref 14. Hydrogen atoms were included in calculated positions 0.96 Å from carbon atoms, with isotropic thermal parameters 1.2 times the equivalent isotropic thermal parameter for the carbon atoms to which they were attached. The weighted least-squares refinement (weights calculated as  $(\sigma^2(F) + g^2F_o^2)^{-1}$ ) converged, with the average shift/esd < 0.025 over the last four cycles.

In the final difference Fourier synthesis, the maximum electron density of  $1.26 \text{ e } \text{Å}^{-3}$  was located  $\sim 0.8$  Å from O2; the minimum was  $-1.46 \text{ e } \text{Å}^{-3}$ . Analysis of variance as a function of Bragg angle, magnitude of  $F_o$ , reflection indices, etc. showed no significant trends.

Tables II and III contain a list of atomic positional parameters and equivalent isotropic thermal parameters and a list of nonroutine interatomic distances and angles, respectively, for  $[\text{TiOTeF}_5(\text{mes})_2]_2\text{mes}$ . Available as supplementary material are lists of anisotropic thermal parameters for all non-hydrogen atoms (Table S-I), hydrogen atom positions and isotropic thermal parameters (Table S-II), C-C distances and C-C-C angles (Table S-III), and observed and calculated structure factors (Table S-IV). (See paragraph at end of paper regarding supplementary material.)

For the thin platelike crystal of  $[\text{Tl}(\text{mes})_2^+][\text{B}(\text{OTeF}_5)_4^-]$ , the  $\theta$ - $2\theta$  scan range was  $[2.0 + 1.0(2\theta_{K\alpha_1} - 2\theta_{K\alpha_2})]^\circ$ , and background measurements were taken for half the total scan time at the scan extremes. The intensities of control reflections (500, 060, 008) monitored every 97 reflections showed a monotonic decrease in intensity for the first 85% of the reflections to 90% of the initial intensity. Deterioration of the control reflections continued at an increased rate for the remainder of the data collection. The final intensities of the control reflections were 75% of their initial intensities. There was no indication of an anisotropic decay in intensity; each control reflection showed similar decay with time. The data were corrected for this decrease in intensity with time.

An analytical absorption correction was calculated for the crystal and applied to the data, resulting in maximum and minimum transmission factors of 0.719 and 0.223, respectively. Lorentz and polarization corrections were applied to the data.

**Table II.** Atomic Coordinates ( $\times 10^4$ ) and Isotropic Thermal Parameters ( $\text{Å}^2 \times 10^3$ ) for  $[\text{TiOTeF}_5(\text{mes})_2]_2\text{mes}^a$

atom	x	y	z	$U_{\text{iso}}^b$
Tl1	581 (1)	3215 (1)	1965 (1)	24 (1)
Tl2	-1881 (1)	1368 (1)	2965 (1)	27 (1)
Te1	1717 (1)	1139 (1)	3053 (1)	29 (1)
O1	444 (7)	1747 (5)	2708 (5)	40 (3)
F1	3027 (7)	504 (5)	3406 (5)	64 (3)
F2	762 (6)	259 (5)	3384 (5)	52 (3)
F3	2016 (7)	1833 (5)	4156 (4)	61 (3)
F4	2900 (6)	1921 (5)	2792 (5)	53 (3)
F5	1667 (7)	307 (5)	2017 (4)	55 (3)
Te2	-2981 (1)	3450 (1)	1856 (1)	30 (1)
O2	-1755 (7)	2806 (6)	2191 (5)	40 (3)
F6	-4261 (6)	4107 (5)	1501 (5)	57 (3)
F7	-4173 (6)	2726 (5)	2168 (5)	52 (3)
F8	-2862 (7)	4310 (5)	2881 (4)	57 (3)
F9	-3364 (7)	2723 (5)	763 (4)	55 (3)
F10	-1996 (7)	4280 (5)	1475 (5)	55 (3)
C1	831 (10)	4398 (7)	3851 (6)	27 (4)
C2	242 (10)	5005 (7)	3422 (7)	27 (4)
C3	808 (11)	5498 (7)	2931 (6)	30 (4)
C4	2067 (11)	5402 (7)	2918 (7)	32 (4)
C5	2699 (11)	4792 (7)	3337 (7)	35 (4)
C6	2054 (12)	4297 (7)	3791 (7)	36 (4)
C7	158 (13)	3853 (8)	4335 (7)	44 (5)
C8	86 (12)	6144 (8)	2448 (8)	44 (5)
C9	4017 (11)	4666 (10)	3264 (10)	60 (6)
C10	-1543 (10)	-385 (7)	1475 (7)	31 (4)
C11	-2136 (11)	-951 (7)	1902 (7)	30 (4)
C12	-1468 (12)	-1640 (8)	2297 (7)	42 (5)
C13	-3377 (10)	-851 (7)	1944 (6)	28 (4)
C14	-4015 (10)	-233 (8)	1551 (7)	34 (4)
C15	-5379 (11)	-131 (10)	1594 (10)	57 (6)
C16	-3415 (10)	314 (7)	1113 (6)	29 (4)
C17	-2187 (11)	232 (7)	1079 (6)	29 (4)
C18	-1515 (12)	810 (8)	569 (8)	44 (5)
C19	2724 (10)	3387 (7)	721 (6)	28 (4)
C20	1970 (10)	4051 (7)	462 (7)	32 (4)
C21	758 (11)	3740 (8)	23 (7)	34 (4)
C22	343 (9)	2806 (8)	-167 (7)	28 (4)
C23	1112 (10)	2185 (8)	93 (7)	31 (4)
C24	2300 (10)	2440 (8)	521 (6)	29 (4)
C25	3155 (11)	1720 (8)	742 (7)	38 (4)
C26	2435 (12)	5058 (8)	624 (8)	44 (5)
C27	-963 (11)	2502 (9)	-643 (8)	46 (5)
C28	-2040 (10)	747 (8)	4854 (7)	35 (4)
C29	-3245 (11)	622 (8)	4463 (7)	39 (5)
C30	-3903 (10)	1389 (9)	4346 (7)	36 (4)
C31	-3305 (11)	2305 (8)	4597 (7)	38 (5)
C32	-2092 (11)	2397 (9)	4972 (6)	37 (4)
C33	-1431 (11)	1641 (8)	5104 (6)	34 (4)
C34	-3917 (13)	-343 (8)	4186 (9)	55 (6)
C35	-93 (12)	1783 (13)	5513 (9)	72 (7)
C36	-3967 (17)	3148 (11)	4486 (10)	80 (8)
C37	4098 (10)	7553 (7)	2777 (7)	30 (4)
C38	4928 (10)	7340 (7)	3424 (7)	31 (4)
C39	5929 (10)	6816 (7)	3267 (6)	30 (4)
C40	6086 (11)	6533 (8)	2437 (7)	36 (4)
C41	5283 (10)	6739 (8)	1776 (7)	32 (4)
C42	4286 (9)	7252 (7)	1947 (7)	27 (4)
C43	3020 (10)	8117 (9)	2969 (8)	44 (5)
C44	6792 (12)	6580 (10)	3984 (8)	55 (6)
C45	5519 (13)	6442 (10)	869 (8)	54 (6)

<sup>a</sup> Estimated standard deviations in the least significant digits are given in parentheses. <sup>b</sup> The equivalent isotropic  $U$  is defined as one-third of the trace of the  $U_{ij}$  tensor.

The thallium and tellurium atoms were located by Patterson methods, and all other non-hydrogen atoms were located in difference Fourier maps, in which phases were determined by the previously located atoms. The refinement involved anisotropic thermal parameters for thallium, tellurium, boron, oxygen, and fluorine atoms. The mesitylene rings were fit to a regular hexagon and refined with anisotropic thermal parameters for all carbon atoms except C8 and C17, which were refined isotropically. Neutral-atom scattering factors were taken from ref 14. The weighted least-squares refinement (weights calculated as  $(\sigma^2(F) + g^2F_o^2)^{-1}$ ) converged, with the average shift/esd < 0.006 over the last eight cycles.

- (13) 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 Nicolet XRD Corp.
- (14) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

**Table III.** Bond Distances (Å) and Angles (deg) for [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub>·mes<sup>a</sup>

Tl1-O1	2.697 (9)	Tl1-O2	2.722 (8)
Tl2-O1	2.719 (8)	Tl2-O2	2.688 (9)
Te1-O1	1.780 (8)	Te1-F1	1.841 (8)
Te1-F2	1.850 (8)	Te1-F3	1.840 (6)
Te1-F4	1.856 (8)	Te1-F5	1.851 (7)
Te2-O2	1.770 (8)	Te2-F6	1.835 (7)
Te2-F7	1.852 (8)	Te2-F8	1.847 (7)
Te2-F9	1.845 (6)	Te2-F10	1.861 (8)
Tl1-C1	3.157 (9)		
Tl1-C2	3.220 (9)	Tl1-C3	3.36 (1)
Tl1-C4	3.45 (1)	Tl1-C5	3.38 (1)
Tl1-C6	3.20 (1)	Tl1-C19	3.39 (1)
Tl1-C20	3.49 (1)	Tl1-C21	3.45 (1)
Tl1-C22	3.37 (1)	Tl1-C23	3.26 (1)
Tl1-C24	3.31 (1)	Tl2-C10	3.22 (1)
Tl2-C11	3.442 (9)	Tl2-C13	3.515 (9)
Tl2-C14	3.44 (1)	Tl2-C16	3.246 (9)
Tl2-C17	3.130 (9)	Tl2-C28	3.43 (1)
Tl2-C29	3.41 (1)	Tl2-C30	3.41 (1)
Tl2-C31	3.38 (1)	Tl2-C32	3.35 (1)
Tl2-C33	3.39 (1)		
O1-Tl1-O2	68.5 (3)	O1-Tl2-O2	68.6 (2)
O1-Te1-F1	179.6 (4)	O1-Te1-F2	94.2 (4)
F1-Te1-F2	85.4 (3)	O1-Te1-F3	95.5 (3)
F1-Te1-F3	84.7 (3)	F2-Te1-F3	89.3 (3)
O1-Te1-F4	95.5 (4)	F1-Te1-F4	84.8 (3)
F2-Te1-F4	170.2 (3)	F3-Te1-F4	89.2 (3)
O1-Te1-F5	95.9 (3)	F1-Te1-F5	83.9 (3)
F2-Te1-F5	89.3 (3)	F3-Te1-F5	168.6 (3)
F4-Te1-F5	90.3 (3)	Tl1-O1-Tl2	111.4 (3)
Tl1-O1-Te1	125.0 (4)	Tl2-O1-Te1	123.5 (4)
O2-Te2-F6	179.4 (3)	O2-Te2-F7	94.6 (4)
F6-Te2-F7	85.1 (3)	O2-Te2-F8	96.1 (3)
F6-Te2-F8	84.5 (3)	F7-Te2-F8	89.8 (3)
O2-Te2-F9	95.5 (3)	F6-Te2-F9	83.9 (3)
F7-Te2-F9	89.0 (3)	F8-Te2-F9	168.4 (3)
O2-Te2-F10	94.7 (4)	F6-Te2-F10	85.6 (3)
F7-Te2-F10	170.7 (3)	F8-Te2-F10	89.8 (3)
F9-Te2-F10	89.5 (3)	Tl1-O2-Tl2	111.5 (3)
Tl1-O2-Te2	121.5 (4)	Tl2-O2-Te2	127.0 (4)

<sup>a</sup> Estimated standard deviations in the least significant digits are given in parentheses. Distances and angles involving carbon atoms only are listed in supplementary material Table S-III.

In the final difference Fourier synthesis, the maximum electron density of 2.88 e Å<sup>-3</sup> was located 0.81 Å from the thallium atom; the minimum was -1.50 e Å<sup>-3</sup>. Analysis of variance as a function of Bragg angle, magnitude of *F*<sub>o</sub>, reflection indices, etc. showed no significant trends.

Tables IV and V contain a list of atomic positional parameters and equivalent isotropic thermal parameters and a list of interatomic distances and angles, respectively, for [Tl(mes)<sub>2</sub><sup>+</sup>][B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup>]. Available as supplementary material are lists of anisotropic thermal parameters for all non-hydrogen atoms (Table S-V), C-C distances and C-C-C angles (Table S-VI), and observed and calculated structure factors (Table S-VII).

## Results and Discussion

**Preparation of Compounds.** The reaction of solid TlF and a toluene solution of the strong acid<sup>10,15,16</sup> HOTeF<sub>5</sub> produces HF and a solution of [TlOTeF<sub>5</sub>(tol)<sub>*x*</sub>]<sub>*y*</sub> (tol = toluene). Superficially, this reaction resembles our previously reported reaction of AgF and HOTeF<sub>5</sub> in toluene.<sup>3</sup> However, there are several important differences. When the respective reaction mixtures are stripped to dryness, removing HF and solvent, the white solid residues that are left are [AgOTeF<sub>5</sub>(tol)<sub>2</sub>]<sub>3</sub> and TlOTeF<sub>5</sub>. That there are no coordinated or lattice toluene molecules in the thallium(I)-containing product was confirmed by the lack of a CH<sub>3</sub> resonance in the <sup>1</sup>H NMR spectrum of a benzene-*d*<sub>6</sub> solution of the white powder. Furthermore, AgF reacts with HOTeF<sub>5</sub> in dichloromethane to produce a solid of composition AgOTeF<sub>5</sub>·CH<sub>2</sub>Cl<sub>2</sub>, but

**Table IV.** Atomic Coordinates (×10<sup>4</sup>) and Isotropic Thermal Parameters (Å<sup>2</sup> × 10<sup>3</sup>) for [Tl(mes)<sub>2</sub><sup>+</sup>][B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup>]<sup>a</sup>

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> <sup>b</sup>
Tl1	2264 (1)	4949 (1)	2744	29 (1)
C1	-675 (10)	3762 (7)	8562 (4)	30 (6)
C2	-82 (10)	3803 (7)	7946 (4)	32 (6)
C3	-686 (10)	3507 (7)	7382 (4)	30 (6)
C4	-1883 (10)	3168 (7)	7433 (4)	25 (5)
C5	-2476 (10)	3127 (7)	8049 (4)	34 (6)
C6	-1872 (10)	3424 (7)	8613 (4)	30 (6)
C7	20 (23)	4035 (12)	9180 (10)	50 (7)
C8	-3792 (18)	2773 (12)	8111 (10)	38 (5) <sup>c</sup>
C9	-10 (19)	3505 (14)	6710 (9)	42 (7)
C10	-2036 (9)	6563 (7)	6742 (5)	32 (6)
C11	-1971 (9)	6936 (7)	7363 (5)	34 (6)
C12	-952 (9)	6784 (7)	7779 (5)	26 (5)
C13	3 (9)	6259 (7)	7574 (5)	35 (6)
C14	-62 (9)	5886 (7)	6953 (5)	35 (6)
C15	-1081 (9)	6038 (7)	6537 (5)	38 (6)
C16	-1215 (26)	5640 (15)	5854 (11)	62 (9)
C17	-3047 (21)	7512 (16)	7602 (12)	55 (6) <sup>c</sup>
C18	1127 (18)	6101 (13)	8003 (11)	47 (7)
Te1	-4095 (1)	5133 (1)	4198 (1)	30 (1)
O1	-4575 (12)	4791 (8)	5020 (6)	35 (4)
F1	-3635 (12)	6113 (8)	4553 (6)	51 (4)
F2	-5645 (11)	5554 (7)	3967 (7)	52 (4)
F3	-3512 (13)	5493 (7)	3402 (6)	54 (4)
F4	-2530 (10)	4747 (8)	4361 (7)	54 (4)
F5	-4490 (12)	4193 (7)	3778 (5)	48 (4)
Te2	-4253 (1)	5007 (1)	1518 (1)	33 (1)
O2	-5532 (12)	4163 (7)	5956 (7)	39 (4)
F6	-4841 (13)	4422 (10)	7145 (6)	71 (6)
F7	-4364 (15)	5538 (10)	6256 (8)	94 (7)
F8	-6723 (17)	5625 (8)	5968 (7)	76 (6)
F9	-7169 (11)	4560 (9)	6866 (6)	54 (5)
F10	-5951 (17)	5810 (8)	7148 (7)	77 (6)
Te3	3501 (1)	7203 (1)	426 (1)	32 (1)
O3	-4815 (12)	3317 (7)	5077 (6)	37 (4)
F11	2907 (11)	8691 (6)	5872 (5)	45 (4)
F12	4304 (11)	7472 (8)	6177 (6)	52 (4)
F13	3930 (11)	6856 (6)	5033 (5)	40 (4)
F14	-2486 (11)	3060 (8)	4730 (6)	53 (4)
F15	2197 (12)	7231 (7)	5768 (8)	61 (5)
Te4	2042 (1)	3560 (1)	4839 (1)	36 (1)
O4	3433 (11)	4183 (7)	4868 (7)	34 (4)
F16	2478 (11)	2907 (7)	5534 (6)	47 (4)
F17	-2745 (17)	7174 (9)	9270 (8)	84 (6)
F18	1462 (11)	4167 (7)	4162 (6)	50 (4)
F19	1223 (13)	4224 (9)	5412 (8)	78 (6)
F20	-9432 (12)	2979 (9)	4806 (10)	88 (7)
B1	-5361 (18)	4104 (15)	5228 (11)	37 (7)

<sup>a</sup> Estimated standard deviations in the least significant digits are given in parentheses. <sup>b</sup> The equivalent isotropic *U* is defined as one-third of the trace of the *U*<sub>*ij*</sub> tensor. <sup>c</sup> These atoms were refined isotropically (see Experimental Section).

TlF does not react with HOTeF<sub>5</sub> in this solvent. The compound TlOTeF<sub>5</sub> is completely insoluble in dichloromethane whereas solutions of AgOTeF<sub>5</sub>·CH<sub>2</sub>Cl<sub>2</sub> exceeding 1 M have been prepared in this solvent.<sup>3</sup>

The coordination of neutral arenes to Tl(I) was first suggested by Auel and Amma in 1968.<sup>17</sup> They isolated benzene complexes of TlAlCl<sub>4</sub> having compositions TlAlCl<sub>4</sub>·1/2C<sub>6</sub>H<sub>6</sub> and TlAlCl<sub>4</sub>·2C<sub>6</sub>H<sub>6</sub>, which readily lost benzene in the solid state. Quite recently, Schmidbauer et al. have isolated and structurally characterized a mesitylene (mes) complex of TlGaBr<sub>4</sub> having the composition [Tl<sub>4</sub>(mes)<sub>6</sub><sup>4+</sup>][GaBr<sub>4</sub>]<sub>4</sub><sup>3-</sup>. This solid also loses all traces of the weakly bound arene ligands under a nitrogen atmosphere or in vacuo. We find that TlOTeF<sub>5</sub> is quite soluble in aromatic hydrocarbons: 0.39 M toluene solutions have been prepared. Of the three solvents benzene, toluene, and mesitylene, we find the highest solubility in toluene and the lowest in benzene. Although the solubility of thallium(I) salts containing weakly coordinating AlCl<sub>4</sub><sup>-</sup> and GaBr<sub>4</sub><sup>-</sup> anions or more strongly coordinating OTeF<sub>5</sub><sup>-</sup>

(15) Poscham, W.; Engelbrecht, A. *Z. Phys. Chem. (Leipzig)* **1971**, *248*, 177.

(16) Rode, B. M.; Engelbrecht, A.; Schantl, J. *Z. Phys. Chem. (Leipzig)* **1973**, *253*, 17.

(17) Auel, T.; Amma, E. L. *J. Am. Chem. Soc.* **1968**, *90*, 5941.

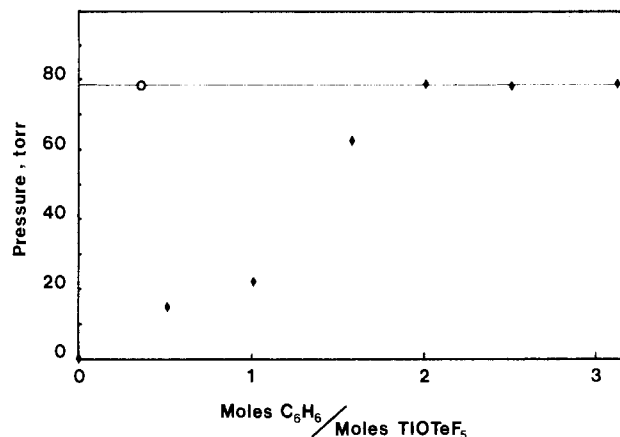
**Table V.** Bond Distances (Å) and Angles (deg) for  $[\text{Ti}(\text{mes})_2]^+[\text{B}(\text{OTeF}_5)_4]^-$ 

Te1-O1	1.82 (1)	Te1-F1	1.82 (1)
Te1-F2	1.85 (1)	Te1-F3	1.82 (1)
Te1-F4	1.81 (1)	Te1-F5	1.81 (1)
O1-B1	1.46 (3)	Te2-O2	1.78 (1)
Te2-F6	1.85 (1)	Te2-F7	1.80 (2)
Te2-F8	1.84 (2)	Te2-F9	1.81 (1)
Te2-F10	1.86 (1)	O2-B1	1.48 (3)
Te3-O3	1.78 (1)	Te3-F11	1.83 (1)
Te3-F12	1.82 (1)	Te3-F13	1.79 (1)
Te3-F14	1.82 (1)	Te3-F15	1.81 (1)
O3-B1	1.45 (3)	Te4-O4	1.80 (1)
Te4-F16	1.82 (1)	Te4-F17	1.82 (2)
Te4-F18	1.80 (1)	Te4-F19	1.81 (2)
Te4-F20	1.84 (1)	O4-B1	1.48 (2)
Tl-C1	3.17 (1)	Tl-C2	3.12 (1)
Tl-C3	3.12 (1)	Tl-C4	3.17 (1)
Tl-C5	3.22 (1)	Tl-C6	3.22 (1)
Tl-C10	3.21 (1)	Tl-C11	3.20 (1)
Tl-C12	3.17 (1)	Tl-C13	3.14 (1)
Tl-C14	3.15 (1)	Tl-C15	3.18 (1)
O1-Te1-F1	89.4 (6)	O1-Te1-F2	95.4 (6)
F1-Te1-F2	90.7 (6)	O1-Te1-F3	176.1 (6)
F1-Te1-F3	88.2 (5)	F2-Te1-F3	87.8 (6)
O1-Te1-F4	89.3 (6)	F1-Te1-F4	89.3 (6)
F2-Te1-F4	175.4 (6)	F3-Te1-F4	87.6 (6)
O1-Te1-F5	95.6 (5)	F1-Te1-F5	174.9 (5)
F2-Te1-F5	89.5 (6)	F3-Te1-F5	86.7 (5)
F4-Te1-F5	90.1 (6)	Te1-O1-B1	131 (1)
O2-Te2-F6	89.0 (6)	O2-Te2-F7	94.9 (7)
F6-Te2-F7	91.3 (7)	O2-Te2-F8	96.8 (6)
F6-Te2-F8	173.8 (6)	F7-Te2-F8	90.4 (7)
O2-Te2-F9	93.2 (6)	F6-Te2-F9	88.5 (6)
F7-Te2-F9	171.8 (7)	F8-Te2-F9	88.9 (7)
O2-Te2-F10	176.3 (6)	F6-Te2-F10	87.6 (7)
F7-Te2-F10	86.5 (7)	F8-Te2-F10	86.6 (6)
F9-Te2-F10	85.3 (7)	B1-O2-Te2	134 (1)
O3-Te3-F11	94.8 (5)	O3-Te3-F12	95.7 (6)
F11-Te3-F13	89.4 (5)	O3-Te3-F13	92.0 (5)
F11-Te3-F13	173.2 (5)	F12-Te3-F13	89.8 (5)
O3-Te3-F14	92.8 (6)	F11-Te3-F14	89.1 (5)
F12-Te3-F14	171.5 (6)	F13-Te3-F14	90.7 (5)
O3-Te3-F15	177.6 (6)	F11-Te3-F15	87.6 (5)
F12-Te3-F15	84.0 (6)	F13-Te3-F15	85.7 (5)
F14-Te3-F15	87.6 (6)	B1-O3-Te3	131 (1)
O4-Te4-F16	95.6 (5)	O4-Te4-F18	89.6 (6)
F16-Te4-F18	174.5 (5)	O4-Te4-F19	92.0 (6)
F16-Te4-F19	89.1 (6)	F18-Te4-F19	89.2 (6)
O4-Te4-F17	93.2 (7)	F16-Te4-F17	89.5 (6)
F18-Te4-F17	91.7 (6)	F19-Te4-F17	174.7 (7)
O4-Te4-F20	176.6 (6)	F16-Te4-F20	86.7 (7)
F18-Te4-F20	88.0 (7)	F19-Te4-F20	85.6 (7)
F17-Te4-F20	89.2 (7)	Te4-O4-B1	133 (1)
O1-B1-O2	108 (2)	O1-B1-O3	113 (2)
O2-B1-O3	108 (2)	O1-B1-O4	107 (2)
O2-B1-O4	112 (1)	O3-B1-O4	109 (2)

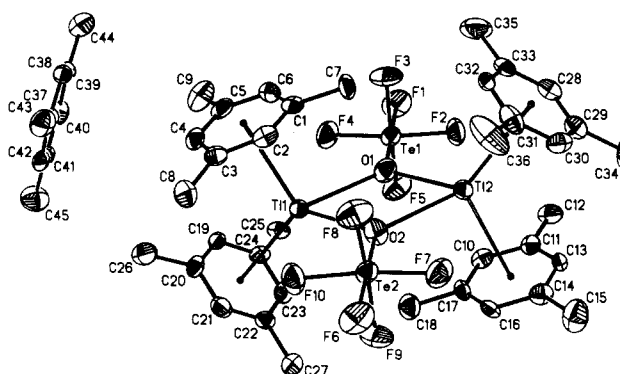
<sup>a</sup> Estimated standard deviations in the least significant digits are given in parentheses. Distances and angles involving carbon atoms only are listed in supplementary material Table S-VI.

anions in aromatic hydrocarbons is now well documented, this behavior is not general. For example, we find that  $\text{TiClO}_4$  is completely insoluble in toluene.

We have measured the apparent molecular weight of  $\text{TiOTeF}_5$  in toluene at 20 °C. Assuming a composition  $[\text{TiOTeF}_5(\text{tol})_x]_y$ , the observed value of  $y$  is 3.4 (7) (average of two determinations). Thus, the complex in solution is oligomeric and may be a mixture of dimers, trimers, tetramers, etc. Upon isolation of a crystalline solid from this solution or from solutions of benzene or mesitylene and drying of the crystals under a nitrogen atmosphere in the glovebox,  $\text{TiOTeF}_5$  is recovered unchanged. This very weak affinity of  $\text{Tl(I)}$  for arene ligands stands in contrast to that of  $\text{Ag(I)}$ : the crystalline solid  $[\text{AgOTeF}_5(\text{tol})_2]_2$  does not liberate toluene even after prolonged vacuum-drying.<sup>3</sup> The weak but finite affinity of  $\text{Tl(I)}$  for benzene can be seen by titrating solid  $\text{TiOTeF}_5$



**Figure 1.** Tensimetric titration of solid  $\text{TiOTeF}_5$  and  $\text{TiClO}_4$  with benzene at 21 °C. The horizontal line at 78.8 Torr represents the vapor pressure of benzene at 21 °C. The diamonds are data for  $\text{TiOTeF}_5$ . The open circle for  $\text{TiClO}_4$  shows no uptake of benzene by this solid.



**Figure 2.** Drawing of the  $[\text{TiOTeF}_5(\text{mes})_2]_2\text{-mes}$  asymmetric unit (50% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

with benzene vapor at 21 °C in a Hg-filled tensimeter.<sup>18</sup> The results are shown in Figure 1. At the benzene/ $\text{TiOTeF}_5$  mole ratio of 1/1, 20 Torr of benzene vapor is observed, showing saturation pressure of 78.8 Torr at the ratio of 2/1 and higher. In sharp contrast to this behavior, solid  $\text{TiClO}_4$  does not interact with benzene: even at a benzene/ $\text{TiClO}_4$  ratio of 0.37, the total pressure of the mixture was identical with the vapor pressure of pure benzene at 21 °C (78.8 Torr).

The striking differences between  $\text{TiOTeF}_5$  and  $\text{TiClO}_4$  underscore the unique structural properties of teflate; it has only one reasonably strong donor atom and cannot form insoluble extended lattices as can perchlorate and sulfonates. While both teflate and perchlorate are derived from strong acids<sup>15,16</sup> and hence are similar electronically, there must be fewer strong thallium-(I)-oxygen bonds in  $\text{TiOTeF}_5$  than in  $\text{TiClO}_4$ . Thus,  $\text{Tl(I)}$  in the former compound is less coordinatively saturated than in the latter. The compounds  $\text{Ti}(\text{OTeF}_5)_4$  and  $\text{Ti}(\text{ClO}_4)_4$  further demonstrate the structural differences between teflate and perchlorate with respect to coordinating ability. The  $\text{Ti(IV)}$  atom in the former compound is probably four-coordinate, since it is volatile and readily adds 2 equiv of  $\text{Cs}^+\text{OTeF}_5^-$  to form  $[\text{Cs}^+]_2[\text{Ti}(\text{OTeF}_5)_6]^{2-}$ .<sup>19</sup> In contrast, the  $\text{Ti(IV)}$  atom in  $\text{Ti}(\text{ClO}_4)_4$  is eight-coordinate.<sup>20</sup>

Cooling a mesitylene solution of  $\text{TiOTeF}_5$  afforded crystals of  $[\text{TiOTeF}_5(\text{mes})_2]_2\text{-mes}$  suitable for diffraction. The addition of  $\text{B}(\text{OTeF}_5)_3$  to a mesitylene solution of  $\text{TiOTeF}_5$  produced  $[\text{Tl}(\text{mes})_2]^+[\text{B}(\text{OTeF}_5)_4]^-$ , which is only sparingly soluble in mesitylene. Recrystallization from mesitylene afforded crystals of this salt suitable for diffraction.

(18) Reference 12, p 58.

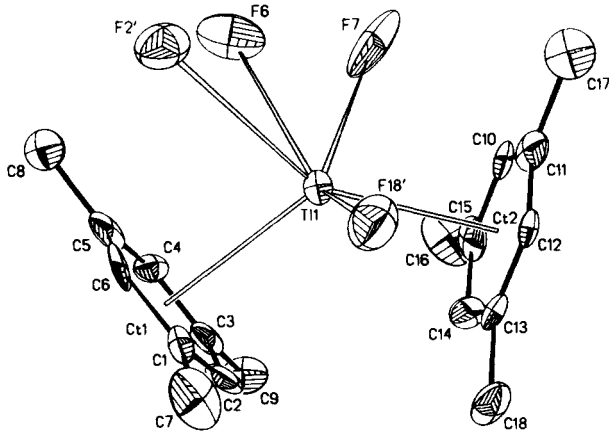
(19) Schröder, K.; Sladky, F. *Chem. Ber.* **1980**, *113*, 1414.

(20) Fourati, M.; Chaabouni, M.; Belin, C. H.; Charbonnel, M.; Pascal, J.-L.; Potier, J. *Inorg. Chem.* **1986**, *25*, 1386.

**Table VI.** Relevant Bond Distances (Å) and Angles (deg) for Compounds with Bridging OTeF<sub>5</sub> Groups (M<sub>2</sub>O<sub>2</sub> Cores)

compd	M-O	M-O-M	O-M-O
[TlOTeF <sub>5</sub> (mes) <sub>2</sub> ] <sub>2</sub> <sup>a</sup>	2.69 (1), 2.70 (1), 2.71 (1), 2.72 (1)	111.5 (4), 111.6 (4)	68.3 (3), 68.5 (3)
[AgOTeF <sub>5</sub> (tol) <sub>2</sub> ] <sub>2</sub> <sup>b</sup>	2.368 (3), 2.396 (3)	101.4 (1)	78.6 (1)
[Au(OTeF <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub> <sup>c</sup>	2.23 (4), 2.29 (4)	101 (2)	75 (1)

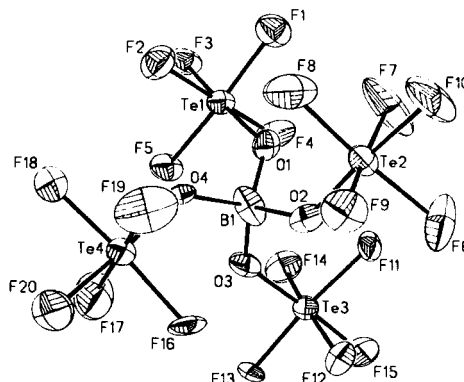
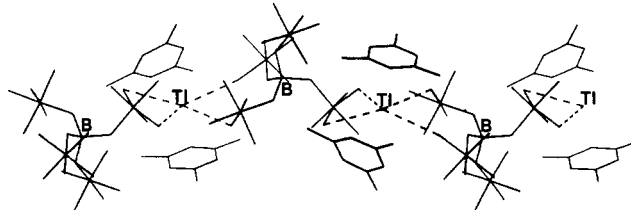
<sup>a</sup>This work; mes = mesitylene. <sup>b</sup>Reference 3; centrosymmetric; tol = toluene. <sup>c</sup>Reference 21; centrosymmetric.

**Figure 3.** Drawing of the Tl(mes)<sub>2</sub><sup>+</sup> cation in [Tl(mes)<sub>2</sub><sup>+</sup>][B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup>] (50% probability ellipsoids). Atoms F18' and F2' are related to F18 and F2 by a symmetry transformation to a second B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> anion.

**Structure of [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub>·mes.<sup>9</sup>** A view of the contents of the asymmetric unit, one dimeric molecule and one occluded mesitylene molecule, is shown in Figure 2 along with the numbering scheme used. Bond distances and angles are collected in Table III. The coordination sphere around each thallium(I) atom is pseudotetrahedral, consisting of two oxygen atoms from two bridging teflate groups and two η<sup>6</sup>-mesitylene molecules. Although the complex has no crystallographically imposed symmetry, it is nearly a centrosymmetric dimer having idealized C<sub>2h</sub> symmetry with the idealized C<sub>2</sub> axis passing through O1 and O2. The four Tl-O bond distances range from 2.69 (1) to 2.72 (1) Å. The O-Tl-O angles are 68.5 (3) and 68.6 (2)° for Tl1 and Tl2, respectively, while the angles formed by the arene centroid-Tl vectors are 118 and 121° for Tl1 and Tl2, respectively.

Along with [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub>, two other compounds have been shown unambiguously to contain bridging teflates.<sup>3,21</sup> Structural data for the three crystallographically characterized complexes with M<sub>2</sub>O<sub>2</sub> cores are listed in Table VI. While this structural feature is unknown for the vast amount of non-metal OTeF<sub>5</sub> chemistry, it is now apparent that teflate can readily bridge two metals.

**Structure of [Tl(mes)<sub>2</sub><sup>+</sup>][B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup>].** The structure of this compound consists of a chain of Tl(mes)<sub>2</sub><sup>+</sup> cations connected by very weak Tl...F interactions with two different B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> anions. Drawings of the cation and anion are shown in Figures 3 and 4, respectively, along with the numbering scheme used. A view of the infinite chain is shown in Figure 5. The mesitylene ligands are η<sup>6</sup>-coordinated to Tl(I) in the Tl(mes)<sub>2</sub><sup>+</sup> cation. The angle formed by the arene centroid-Tl vectors is 129° in this salt. The dihedral angle formed by the two mesitylene planes in the Tl(mes)<sub>2</sub><sup>+</sup> cation is 55.8°. The geometry around the boron atom of the B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> anion is tetrahedral, with the six O-B-O bond angles ranging from 107 (2) to 113 (1)°. The B-O bond lengths are longer and the Te-O bond lengths are shorter (averages are 1.48 (2) and 1.80 (1) Å, respectively) than the respective bond lengths in B(OTeF<sub>5</sub>)<sub>3</sub> (1.358 (6) and 1.874 (6) Å).<sup>23</sup> These

**Figure 4.** Drawing of the B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> anion in [Tl(mes)<sub>2</sub><sup>+</sup>][B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup>] (50% probability ellipsoids).**Figure 5.** Infinite-chain structure of [Tl(mes)<sub>2</sub><sup>+</sup>][B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup>].

differences are expected and will be discussed below along with the spectroscopic data for these compounds. The four OTeF<sub>5</sub> groups in the B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> anion fit together without any distortions from "normal" teflate geometry;<sup>24</sup> all O-Te-F angles are a few degrees greater than 90°, and the B-O-Te angles, which range from 131 (1) to 134 (1)°, are not greater than the 132.3 (4)° angle in B(OTeF<sub>5</sub>)<sub>3</sub>.<sup>23</sup> The closest F...F distance between teflate groups is 2.87 (2) Å for F4...F14; F...F distances within each teflate groups are 2.5-2.6 Å.

**Comparison of [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub> with [Tl<sub>4</sub>(mes)<sub>6</sub><sup>4+</sup>][GaBr<sub>4</sub><sup>-</sup>]<sub>4</sub>.** As discussed above, the weak interaction between neutral arenes and Tl(I) has long been documented. Nevertheless, prior to this work the only structurally characterized Tl(I)-neutral arene complex was [Tl<sub>4</sub>(mes)<sub>6</sub><sup>4+</sup>][GaBr<sub>4</sub><sup>-</sup>]<sub>4</sub>.<sup>8</sup> This tetrameric compound consists of two Tl(mes)<sup>+</sup> and two Tl(mes)<sub>2</sub><sup>+</sup> cations bridged in a complicated way by four GaBr<sub>4</sub><sup>-</sup> anions. In both types of cations, the mesitylene molecules are η<sup>6</sup>-coordinated to Tl(I).

The two symmetry-related Tl(mes)<sub>2</sub><sup>+</sup> units in [Tl<sub>4</sub>(mes)<sub>6</sub><sup>4+</sup>][GaBr<sub>4</sub><sup>-</sup>]<sub>4</sub> and the two independent Tl(mes)<sub>2</sub><sup>+</sup> units in [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub> are structurally very similar. If one averages the Tl-C bond distances for each η<sup>6</sup>-mesitylene ligand, the values for the Tl(mes)<sub>2</sub><sup>+</sup> units in [Tl<sub>4</sub>(mes)<sub>6</sub><sup>4+</sup>][GaBr<sub>4</sub><sup>-</sup>]<sub>4</sub> are 3.32 and 3.34 Å<sup>8</sup> while in [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub> they are 3.29 (12), 3.33 (15), 3.38 (9), and 3.39 (3) Å for the mesitylene molecules containing C1, C10, C19, and C28, respectively.<sup>25</sup> The dihedral angles formed by the planes of the mesitylene ligands in each Tl(mes)<sub>2</sub><sup>+</sup> unit are 60.5° for [Tl<sub>4</sub>(mes)<sub>6</sub><sup>4+</sup>][GaBr<sub>4</sub><sup>-</sup>]<sub>4</sub>,<sup>9</sup> 51.5° for Tl1, and 49.0° for Tl2. The small differences between the two compounds are probably the consequence of the number of anion atoms coordinated to each Tl(I) atom: only two oxygen atoms in [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub> vs. four bromine atoms for the Tl(mes)<sub>2</sub><sup>+</sup> units in [Tl<sub>4</sub>(mes)<sub>6</sub><sup>4+</sup>][GaBr<sub>4</sub><sup>-</sup>]<sub>4</sub>.<sup>8</sup>

Although the best description of the arene ligand coordination in [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub> is η<sup>6</sup>, note that the Tl-C bond distances for any one mesitylene ligand vary over a range of values. The smallest range involves the ring containing C28 (Tl-C = 3.36 (1)-3.43 (1) Å) while the largest involves the ring containing C10 (Tl-C = 3.14 (1)-3.52 (1) Å). We suggest that this variation

(21) Huppman, P.; Hartl, H.; Seppelt, K. *Z. Anorg. Allg. Chem.* **1985**, *524*, 26.

(22) (a) Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 877. (b) Engelbrecht, A.; Sladky, F. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 189. (c) Seppelt, K. *Acc. Chem. Res.* **1979**, *12*, 211.

(23) Sawyer, J. F.; Schrobilgen, G. J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 1561.

(24) For a complete list of all OTeF<sub>5</sub> structures to date see ref 10.

(25) Rms values are shown in parentheses for our average Tl-C bond distances: the individual Tl-C bond distances have not yet been reported for [Tl<sub>4</sub>(mes)<sub>6</sub><sup>4+</sup>][GaBr<sub>4</sub><sup>-</sup>]<sub>4</sub>.<sup>8</sup>

**Table VII.** Infrared and Raman Spectral Data<sup>a</sup>

compd	medium	$\nu(\text{TeO})$		$\nu(\text{TeF})$	
		IR	Raman	IR	Raman
TlOTeF <sub>5</sub>	solid	831	844	650 bd	647, 669
	toluene	813			
[TlOTeF <sub>5</sub> (mes) <sub>2</sub> ] <sub>2</sub> <sup>b</sup>	solid	820	826	660 bd	664
[Tl(mes) <sub>2</sub> ] <sup>+</sup> [B(OTeF <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>	solid	797, 715 bd		675, 630	
[N( <i>n</i> -Bu) <sub>4</sub> ] <sup>+</sup> [B(OTeF <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup>	solid	797, 712 bd		673, 640	
[Cs <sup>+</sup> ][B(OTeF <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup> <sup>c</sup>	acetonitrile	795, 720		675	
[AgOTeF <sub>5</sub> (tol) <sub>2</sub> ] <sub>2</sub> <sup>d</sup>	solid	819	836		
[N( <i>n</i> -Bu) <sub>4</sub> ] <sup>+</sup> [H(OTeF <sub>5</sub> ) <sub>2</sub> ] <sup>-</sup> <sup>e</sup>	solid	766	850		

<sup>a</sup>All data are in cm<sup>-1</sup>; all data from this work unless noted otherwise. <sup>b</sup>mes = mesitylene. <sup>c</sup>Reference 11. <sup>d</sup>Reference 3; tol = toluene. <sup>e</sup>Reference 10.

is the consequence of nonbonded interactions between the mesitylene rings on a given Tl(I) atom instead of some intrinsic electronic effect. For the ring containing C10, for example, the Tl-C distances to the carbon atoms closest to the ring containing C28 are 3.44 (1) (Tl2-C11), 3.52 (1) (Tl2-C13), and 3.44 (1) Å (Tl2-C14), while the other three Tl-C distances are 3.22 (1) (Tl2-C10), 3.25 (1) (Tl2-C16), and 3.13 (1) Å (Tl2-C17). As in [Tl<sub>4</sub>(mes)<sub>6</sub>]<sup>4+</sup>[GaBr<sub>4</sub>]<sup>-</sup>,<sup>8</sup> no stereochemical activity of the 6s<sup>2</sup> electron pair is recognizable in the coordination spheres of Tl1 and Tl2.

**Comparison of [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub> with [Tl(mes)<sub>2</sub>]<sup>+</sup>[B(OTeF<sub>5</sub>)<sub>4</sub>]<sup>-</sup>.** The Tl(mes)<sub>2</sub><sup>+</sup> moieties in both of these compounds are similar to each other and to the Tl(mes)<sub>2</sub><sup>+</sup> units in [Tl<sub>4</sub>(mes)<sub>6</sub>]<sup>4+</sup>[GaBr<sub>4</sub>]<sup>-</sup>. For all three compounds, the dihedral angles formed by the planes of the mesitylene ligands in each cation fall within a narrow range (49–60°, see above). As in [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub>, the Tl-C distances for each mesitylene ligand in [Tl(mes)<sub>2</sub>]<sup>+</sup>[B(OTeF<sub>5</sub>)<sub>4</sub>]<sup>-</sup> vary over a range of values, 3.12 (1)–3.22 (1) Å for the ring containing C1 and 3.14 (1)–3.21 (1) Å for the ring containing C10. As discussed above, nonbonded interactions are probably the cause of this minor departure from ideal η<sup>6</sup> coordination.

The average Tl-C distance of 3.17 Å in [Tl(mes)<sub>2</sub>]<sup>+</sup>[B(OTeF<sub>5</sub>)<sub>4</sub>]<sup>-</sup> is substantially shorter than the average of 3.35 Å for [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub>; the difference is more than 10 times the estimated standard deviations for the individual Tl-C distances in [Tl(mes)<sub>2</sub>]<sup>+</sup>[B(OTeF<sub>5</sub>)<sub>4</sub>]<sup>-</sup>. Compared with that of [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub>, the stronger coordination of mesitylene to Tl(I) in [Tl(mes)<sub>2</sub>]<sup>+</sup>[B(OTeF<sub>5</sub>)<sub>4</sub>]<sup>-</sup> is a clear indication of the weaker interaction of Tl(I) with its counterion. The B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> anion is extremely weakly coordinated to Tl(I) in [Tl(mes)<sub>2</sub>]<sup>+</sup>[B(OTeF<sub>5</sub>)<sub>4</sub>]<sup>-</sup>. The shortest Tl...F distances in this salt are 3.17 (1) Å to F6, 3.25 (1) Å to F18', 3.47 (1) Å to F2', and 3.83 (2) Å to F7. The first two of these distances are barely shorter than the 3.35 Å sum of the van der Waals radii for thallium (2.00 Å) and fluorine (1.35 Å).<sup>26,27</sup> Note that the shortest Tl...F distances in [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub>, which are arguably nonbonded contacts, are just longer than the 3.35-Å van der Waals limit; they are 3.378 (7), 3.454 (7), 3.529 (7), and 3.550 (7) Å for F10, F2, F4, and F7, respectively. In contrast, the Tl-O distances in [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub> are all ~2.70 Å.

Ab initio calculations on OTeF<sub>5</sub><sup>-</sup> and other teflate species suggest that the amount of negative charge on the fluorine atoms of B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> is only about one-tenth the amount on the fluorine atoms of SbF<sub>6</sub><sup>-</sup>.<sup>28</sup> Note that the four weakly interacting fluorine atoms in [Tl(mes)<sub>2</sub>]<sup>+</sup>[B(OTeF<sub>5</sub>)<sub>4</sub>]<sup>-</sup> all occupy equatorial positions in their respective OTeF<sub>5</sub> groups. It is not apparent whether this is the result of steric or electronic factors. The bonds between these fluorine atoms and their respective tellurium atoms are not significantly longer than the other Te-F bond distances in the

**Table VIII.** Spectroscopic and Structural Data for Representative OTeF<sub>5</sub> Compounds<sup>a</sup>

compd	$\nu(\text{TeO})$ , <sup>b</sup> cm <sup>-1</sup>	Te-O, <sup>c</sup> Å	$\delta_A$ <sup>d</sup>
B(OTeF <sub>5</sub> ) <sub>3</sub>	<740 <sup>e</sup>	1.874 (6) <sup>f</sup>	-46.2 <sup>g</sup>
HOTeF <sub>5</sub>	734 <sup>g,h</sup>		-42.4 <sup>g</sup>
[Tl(mes) <sub>2</sub> ] <sup>+</sup> [B(OTeF <sub>5</sub> ) <sub>4</sub> ] <sup>-</sup> <sup>i</sup>	736 <sup>j</sup>	1.80 (2)	-38.3
[N( <i>n</i> -Bu) <sub>4</sub> ] <sup>+</sup> [H(OTeF <sub>5</sub> ) <sub>2</sub> ] <sup>-</sup>	808 <sup>g,k</sup>	1.800 (4) <sup>g,l</sup> (1.842 <sup>m</sup> )	-32.0 <sup>g</sup>
[TlOTeF <sub>5</sub> (mes) <sub>2</sub> ] <sub>2</sub>	823 <sup>n</sup>	1.774 (8) <sup>o</sup>	-23.5 <sup>p</sup>
Mn(CO) <sub>5</sub> (OTeF <sub>5</sub> )	848 <sup>q</sup>	1.75 (1) <sup>q</sup> (1.83 <sup>q</sup> )	-30.8 <sup>q</sup>
[C <sub>14</sub> H <sub>19</sub> N <sub>2</sub> ] <sup>+</sup> [OTeF <sub>5</sub> ] <sup>-</sup> <sup>r</sup>	865 <sup>s</sup>	1.781 (2) <sup>s</sup> (1.798) <sup>s</sup>	-20.0 <sup>s</sup>
[N( <i>n</i> -Bu) <sub>4</sub> ] <sup>+</sup> [OTeF <sub>5</sub> ] <sup>-</sup>	867 <sup>g</sup>		-19.0 <sup>g</sup>

<sup>a</sup>All data from this work unless otherwise noted. <sup>b</sup>Solid-state IR data unless otherwise noted. <sup>c</sup>The value in parentheses is corrected for librational motion of the OTeF<sub>5</sub> group. <sup>d</sup><sup>19</sup>F chemical shift (CH<sub>2</sub>Cl<sub>2</sub>, 22 °C, CFCl<sub>3</sub> internal standard) of fluorine trans to oxygen. <sup>e</sup>Highest energy band attributable to  $\nu(\text{TeO})$  or  $\nu(\text{TeF})$ ; ref 11. <sup>f</sup>Reference 23. <sup>g</sup>Reference 10. <sup>h</sup>Gas-phase spectrum; this single band is a combination of  $\nu(\text{TeO})$  and  $\nu(\text{TeF})$ . <sup>i</sup>mes = mesitylene. <sup>j</sup>Weighted average of  $\nu(\text{TeO})$  bands at 797 (A<sub>1</sub>) and 715 cm<sup>-1</sup> (T<sub>2</sub>). <sup>k</sup>Average of  $\nu(\text{TeO})$  bands at 850 and 766 cm<sup>-1</sup>. <sup>l</sup>Average of 1.798 (4) and 1.802 (4) Å. <sup>m</sup>Average of 1.841 and 1.843 Å. <sup>n</sup>Average of  $\nu(\text{TeO})$  bands at 820 (IR) and 826 cm<sup>-1</sup> (Raman). <sup>o</sup>Average of 1.769 (8) and 1.779 (8) Å. <sup>p</sup>Solvent is mesitylene. <sup>q</sup>Reference 2. <sup>r</sup>[C<sub>14</sub>H<sub>19</sub>N<sub>2</sub>]<sup>+</sup> is the protonated form of 1,8-bis(dimethylamino)naphthalene (Proton Sponge; Aldrich). <sup>s</sup>Reference 28.

B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> anion. Generally, coordination of an anion such as SbF<sub>6</sub><sup>-</sup> produces a longer Sb-F bond distance to the bridging fluorine atom,<sup>6e</sup> but this is not always the case.<sup>6d</sup>

Consistent with the stronger Tl-C bonds in [Tl(mes)<sub>2</sub>]<sup>+</sup>[B(OTeF<sub>5</sub>)<sub>4</sub>]<sup>-</sup> as compared with [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub>, the mesitylene ligands are much more difficult to remove from the former than from the latter. After 6 weeks of vacuum-drying (10<sup>-5</sup> Torr) at room temperature, all of the mesitylene had not been removed from a sample of [Tl(mes)<sub>2</sub>]<sup>+</sup>[B(OTeF<sub>5</sub>)<sub>4</sub>]<sup>-</sup>. In contrast, [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub>-mes loses all traces of mesitylene under these conditions within 3 days. The inability to isolate Tl<sup>+</sup>B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> in pure form has precluded a quantitative benzene vapor titration of this putative salt. However, addition of 0.5 equiv of benzene vapor (based on Tl(I)) to a sample of [Tl(mes)<sub>2</sub>]<sup>+</sup>[B(OTeF<sub>5</sub>)<sub>4</sub>]<sup>-</sup> that had lost almost all of its mesitylene under vacuum resulted in a vapor pressure of 0 Torr. In contrast, the same experiment with TlOTeF<sub>5</sub> resulted in a vapor pressure of 15 Torr (see Figure 1).

**Spectroscopic Data.** We have recently reviewed the data illustrating that the Te-O bond distance, the Te-O stretching frequency ( $\nu(\text{TeO})$ ), and the <sup>19</sup>F NMR chemical shift of the fluorine atom trans to oxygen ( $\delta_A$ ) are all strongly correlated for OTeF<sub>5</sub> compounds.<sup>3,10</sup> We have also shown that centrosymmetric or nearly centrosymmetric molecules containing two teflate groups exhibit an IR  $\nu(\text{TeO})$  band and a Raman  $\nu(\text{TeO})$  band that are mutually exclusive (i.e., the Te-O oscillators are vibrationally coupled).<sup>3,10</sup>

Infrared and Raman spectral data for TlOTeF<sub>5</sub>, [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub>, and [Tl(mes)<sub>2</sub>]<sup>+</sup>[B(OTeF<sub>5</sub>)<sub>4</sub>]<sup>-</sup> are listed in Table VII, along with pertinent data for other compounds. The data for

(26) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; p 260.

(27) Bondi, A. J. *Phys. Chem.* **1964**, *68*, 441.

(28) Miller, P. K.; Abney, K. D.; Rappé, A. K.; Swanson, B. I.; Anderson, O. P.; Strauss, S. H., manuscript in preparation. The fluorine basis set used for these calculations was the one developed for TeF<sub>6</sub> (Rappé, A. K. *J. Chem. Phys.* **1986**, *85*, 6576). The oxygen basis set was valence-double- $\zeta$  plus d functions plus a set of diffuse s and p functions. Hartree-Fock analytic gradients were used to optimize the geometries.

[TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub> and [Tl(mes)<sub>2</sub><sup>+</sup>][B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup>] are in harmony with the molecular structures for these compounds. There are mutually exclusive IR and Raman  $\nu(\text{TeO})$  bands for [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub>, consistent with the nearly centrosymmetric structure of this dimer. The average  $\nu(\text{TeO})$  value of 823 cm<sup>-1</sup> is between the low value for HOTeF<sub>5</sub> (733 cm<sup>-1</sup>) and the high value for [N(*n*-Bu)<sub>4</sub><sup>+</sup>][OTeF<sub>5</sub><sup>-</sup>] (867 cm<sup>-1</sup>) and correlates well with the Te-O distances and  $\delta_A$  for this compound (Table VIII). The compound TlOTeF<sub>5</sub> also exhibits mutually exclusive IR and Raman  $\nu(\text{TeO})$  bands. While little is known about the structure of this compound, the vibrational data indicate that it probably contains bridging OTeF<sub>5</sub> groups in the solid state.

A comparison of structural and spectroscopic data for the B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> anion and for B(OTeF<sub>5</sub>)<sub>3</sub><sup>11,23</sup> shows the expected trends. For example, the strong B-O bonds in B(OTeF<sub>5</sub>)<sub>3</sub>, with some degree of p-p  $\pi$  character, are consistent with weaker and longer Te-O bonds than found in the B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> anion. The bands at 797 and 715 cm<sup>-1</sup> for [Tl(mes)<sub>2</sub><sup>+</sup>][B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup>] are tentatively assigned to the "A<sub>1</sub>" and "T<sub>2</sub>" stretching normal modes for the four Te-O oscillators in the B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> anion. The symmetric stretch at 797 cm<sup>-1</sup> is IR active (albeit weak) presumably because the B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> anion does not possess strict T<sub>d</sub> symmetry.

We have examined the <sup>19</sup>F NMR spectra of [N(*n*-Bu)<sub>4</sub><sup>+</sup>][B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup>] and [Tl(mes)<sub>2</sub><sup>+</sup>][B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup>] in dichloromethane at two different concentrations (see Experimental Section). There is a very slight cation dependence on  $\delta_A$  for the B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> anion and a smaller concentration dependence. These data demonstrate that some degree of ion pairing, whether specific or nonspecific, occurs for salts of B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> in dichloromethane solution. Differences in cation-fluorine interactions for [N(*n*-Bu)<sub>4</sub><sup>+</sup>][B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup>] and [Tl(mes)<sub>2</sub><sup>+</sup>][B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup>] in the solid state could potentially be probed by Raman spectroscopy, since OTeF<sub>5</sub> compounds generally exhibit strong, sharp  $\nu(\text{TeF})$  bands.<sup>22</sup> The

positions of these bands are sensitive to the environment of the OTeF<sub>5</sub> group(s).<sup>22</sup> However, both B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> salts undergo photoinduced decomposition in the Raman spectrometer laser beam.

**Conclusions.** The compound [Tl(mes)<sub>2</sub><sup>+</sup>][B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup>] has been prepared and fully characterized. Structural and spectroscopic data show that the B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> anion is extremely weakly coordinated to Tl(mes)<sub>2</sub><sup>+</sup> in the solid state and in solution. This compound has already proven to be a useful reagent for introducing the B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> anion by means of metathetical reactions of [Tl(mes)<sub>2</sub><sup>+</sup>][B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup>] with metal and non-metal chlorides.<sup>29</sup> We intend to prepare a variety of salts of this anion with coordinatively unsaturated cations such as Fe(porphyrin)<sup>+</sup> and SiR<sub>3</sub><sup>+</sup>. While there may be no such thing as a noncoordinating anion in condensed media, we propose that the B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup> anion is an excellent candidate for the least coordinating anion.

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**Supplementary Material Available:** Listings of anisotropic thermal parameters for all non-hydrogen atoms (Table S-I), hydrogen atom positions and isotropic thermal parameters (Table S-II), and C-C distances and C-C-C angles (Table S-III) for [TlOTeF<sub>5</sub>(mes)<sub>2</sub>]<sub>2</sub> and listings of anisotropic thermal parameters for all non-hydrogen atoms (Table S-V) and C-C distances and C-C-C angles (Table S-VI) for [Tl(mes)<sub>2</sub><sup>+</sup>][B(OTeF<sub>5</sub>)<sub>4</sub><sup>-</sup>] (12 pages); listings of observed and calculated structure factors for both compounds (Tables S-IV and S-VII) (63 pages). Ordering information is given on any masthead page.

(29) Strauss, S. H.; Noiro, M. D., unpublished observations, 1986.

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## Controlled Hydrolysis of the Hexafluorides of Molybdenum, Tungsten, and Rhenium: Structure of Oxonium ( $\mu$ -Fluoro)bis(tetrafluorooxotungstate(VI))

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The controlled hydrolysis reactions of the hexafluorides of molybdenum, tungsten, and rhenium in anhydrous hydrogen fluoride are reported. Vibrational spectra indicate that the hydrolysis of MoF<sub>6</sub> yields solely MoOF<sub>4</sub>, as previously believed. Hydrolysis of ReF<sub>6</sub> yields a mixture of ReOF<sub>4</sub> and H<sub>3</sub>O<sup>+</sup>Re<sub>2</sub>O<sub>2</sub>F<sub>9</sub><sup>-</sup>, while WF<sub>6</sub> hydrolyzes to give only H<sub>3</sub>O<sup>+</sup>W<sub>2</sub>O<sub>2</sub>F<sub>9</sub><sup>-</sup>, even with excess WF<sub>6</sub>. These reactions suggest that WOF<sub>4</sub> is a stronger Lewis acid than MoOF<sub>4</sub>. H<sub>3</sub>O<sup>+</sup>W<sub>2</sub>O<sub>2</sub>F<sub>9</sub><sup>-</sup> crystallizes in the monoclinic space group P2<sub>1</sub>/n (a nonstandard setting of P2<sub>1</sub>/c, No. 13). At 293 K, *a* = 14.818 (3) Å, *b* = 5.198 (1) Å, *c* = 5.576 (1) Å,  $\beta$  = 94.41 (1)°, *V* = 428.2 Å<sup>3</sup>, and *Z* = 2. Refinement converged with *R* = 0.090, and *R*<sub>w</sub> = 0.098 for 784 independent observed X-ray diffraction reflections. The structure consists of discrete ions with a fluorine-bridged W<sub>2</sub>O<sub>2</sub>F<sub>9</sub><sup>-</sup> anion. The angle at the bridge is 144 (2)° with the bridging W-F distance being 2.13 (1) Å. The average terminal W-F distance is 1.86 (2) Å, and W=O, being trans to the bridge, is 1.57 (3) Å. The fluorine and oxygen atoms are approximately hexagonally close packed.

### Introduction

Some controlled hydrolysis reactions of several transition-metal hexafluorides in anhydrous hydrogen fluoride have been reported previously.<sup>1-4</sup> The products obtained were classified according to the electron affinities of each hexafluoride. The hexafluorides

of Ir, Pt, and Ru have high electron affinity and oxidize water to form oxonium salts of the type H<sub>3</sub>O<sup>+</sup>MF<sub>6</sub><sup>-</sup> or (H<sub>3</sub>O<sup>+</sup>)<sub>2</sub>MF<sub>6</sub><sup>2-</sup>, while the low electron affinity hexafluorides of Mo, Re, Os, U and Np undergo fluorine substitution to form the metal oxide tetrafluorides. The latter reaction has provided a useful alternative to the thermal synthesis methods<sup>5</sup> often used to prepare some of these oxide tetrafluorides. The controlled hydrolysis of WF<sub>6</sub> has been found to give a product different from those described above. On the basis of vibrational spectra and elemental analyses, the

(1) Selig, H.; Sunder, W. A.; Disalvo, F. A.; Falconer, W. E. *J. Fluorine Chem.* 1978, 11, 39.

(2) Selig, H.; Sunder, W. A.; Schilling, F. C.; Falconer, W. E. *J. Fluorine Chem.* 1978, 11, 629.

(3) Wilson, P. W. *J. Chem. Soc., Chem. Commun.* 1972, 1241.

(4) Peacock, R. D.; Edelstein, N. *J. Inorg. Nucl. Chem.* 1976, 38, 771.

(5) Cady, G. H.; Hargreaves, G. B. *J. Chem. Soc.* 1961, 1568.