Table VII. Secondary Contacts to the Sb(III) AX_4E Polyhedron in $Sb_3F_{14}^-$ Anions

compound	face capping	edge bridging
$(S_4N_4)(Sb_3F_{14})(SbF_6)$[a]	4	0
$(S_8)(Sb_3F_{14})(SbF_6)$[b]	4	2
$(Te_2Se_2)(Sb_3Fe_{14})(SbF_6)$[c]	0	4
$(Te_2Se_4)(Sb_3F_{14})(SbF_6)$[d]	3	2
$(Te_{3.0}Se_{1.0})(Sb_3F_{14})(SbF_6)$[c]	4	0

[a] Reference 21. [b] Reference 22. [c] This work. [d] Reference 13.

less than the sum of the appropriate van der Waals radii.[28] As in all of the homopolyatomic M_4^{2+} cations all four edges of the cations are bridged by fluorine atoms, and there are also several contacts approximately along the diagonals of the square-planar cations (Figure 1). In $(Te_2Se_2)(Sb_3F_{14})(SbF_6)$ the edge-bridging contacts are unsymmetrical and involve atoms F(21) and F(41), which are 0.46 and 0.93 Å respectively out of the plane of the *trans*-$Te_2Se_2^{2+}$ cation. In addition the contact Te(1)···F(33) is along the extension of the Te···Te diagonal of the cation [Te(1)′···Te(1)···F(33) is 176.7 (9)°] with the atom F(33) 0.17 Å out of the plane of the cation. These contacts are ca. 0.75–0.55 Å shorter than the sum of the neutral-atom van der Waals radii. The edges of the averaged cation $Te_{3.0}Se_{1.0}^{2+}$ are symmetrically bridged by the atoms F(13), F(22), F(42), and F(44). These bridging distances vary from 2.85 to 3.40 Å and are quite similar in length to the contacts in $Te_4(SbF_6)_2$.[9] They do however, lie significantly (0.73–1.54 Å) out of the average plane of the cation. The remaining contacts are more irregular (Figure 1). The contacts Te(1)···F(45), Te(3)···F(15), and Te(4)···F(12) could possibly be regarded as being analogous to the "diagonal" contacts in $Te_2Se_2^{2+}$. These anion–cation contacts can be regarded as being nucleophilic and involve the donation of electron density from fluorine atoms into the lowest unoccupied MO's of the cation. The analogous interactions in the homopolyatomic cations M_4^{2+} (M = S, Se and Te) are discussed more extensively elsewhere.[9]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work, Dr. J. E. Vekris for preparing the Te–Se alloy, and Dr. G. J. Schrobilgen for valuable assistance with the ^{77}Se NMR measurements.

Registry No. *trans*-$(Te_2Se_2)(Sb_3F_{14})(SbF_6)$, 68791-83-3; $(Te_{3.0}Se_{1.0})(Sb_3F_{14})(SbF_6)$, 98587-07-6; Te, 13494-80-9; Se, 7782-49-2; SbF_5, 7783-70-2.

Supplementary Material Available: A comparison of the geometries of the known $Sb_3F_{14}^-$ anions (Table VI), listings of anisotropic thermal parameters (Table VIII), bond distances and bond angles in the $Sb_3F_{14}^-$ and SbF_6^- anions (Table IX), and final structure factor amplitudes (Table X), and drawings of the crystal packing in $(Te_2Se_2)(Sb_3F_{14})(SbF_6)$ (Figure 5) and $(Te_{3.0}Se_{1.0})(Sb_3F_{14})(SbF_6)$ (Figure 6) (51 pages). Ordering information is given on any current masthead page.

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Preparation and Characterization of Silver(I) Teflate Complexes: Bridging $OTeF_5$ Groups in the Solid State and in Solution

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The preparations of $AgOTeF_5{\cdot}CH_2Cl_2$ and $[AgOTeF_5(C_6H_5CH_3)_2]_2$ are reported. The latter compound crystallizes in the monoclinic system, space group $P2_1/c$ (No. 14). Unit cell parameters are $a = 9.363$ (2) Å, $b = 18.109$ (4) Å, $c = 10.514$ (2) Å, $\beta = 112.89$ (2)°, and $Z = 2$. The centrosymmetric dimeric molecules contain planar Ag_2O_2 cores, with two $OTeF_5$ groups bridging two silver atoms. A molecular weight determination demonstrates that the compound is also dimeric in toluene solution. The Ag–O and Ag–O′ bond distances are 2.396 (3) and 2.368 (3) Å, respectively. The Ag–O–Ag′ and O–Ag–O′ bond angles are 101.4 (1) and 78.6 (1)°, respectively. Structural and spectroscopic data indicate that the silver(I)–oxygen bonds in this compound have a large amount of ionic character. Spectroscopic data indicate that $AgOTeF_5{\cdot}CH_2Cl_2$ and the literature compound $AgOTeF_5(CH_3CN)_x$ also contain bridging $OTeF_5$ groups in the solid state. These data provide the first evidence that the $OTeF_5$ group can bridge two elements in the solid state and in solution. Our structure also demonstrates that teflate is a much stronger ligand than perchlorate in this type of complex. This is the first direct comparison of the ligating ability of teflate to another monovalent oxoanion.

Introduction

Pentafluoroorthotellurate ($OTeF_5^-$), or teflate, has only recently been used as a ligand for high-valent[1] and low-valent[2,3] transition-metal chemistry. This bulky[4–6] and electronegative[7] pseudohalide holds the promise of inducing coordinative unsaturation by means of nonbonded interactions with other ligands in a metal complex. In addition, coordinative unsaturation may be realized because of the inability of this bulky, unidentate anion to form extended lattices. To facilitate the synthesis of a wide vareity of metal teflates, we have prepared silver(I) teflate, $AgOTeF_5$, as a halide/$OTeF_5^-$ metathesis reagent. A material prepared earlier by Sladky et al.[8,9] and formulated by them as $AgOTeF_5(CH_3CN)_x$ is less useful for generating coordinatively unsaturated complexes because it contains several equivalents of the two-electron donor acetonitrile.

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(4) The ionic radius of the teflate anion has been estimated to be 2.3–2.4 Å from crystallographic data for the K^+, Rb^+, and Cs^+ salts[5] (cf. I^-, 2.12 Å[6]).

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In this paper we describe the preparation and characterization of $AgOTeF_5$ and its bis(toluene) adduct. An X-ray structural determination shows that the latter compound is a dimer with two $OTeF_5$ groups bridging two silver atoms, producing a centrosymmetric Ag_2O_2 core. A molecular weight determination shows that this compound is also dimeric in toluene solution. Vibrational spectroscopic data suggest that $AgOTeF_5$ and $AgOTeF_5(CH_3CN)_x$ also contain bridging teflate groups. Despite the large amount of main-group $OTeF_5$ chemistry studied during the past 20 years,[10] this paper reports the first evidence that teflate can bridge two elements in the solid state and in solution. While this work was in progress, we learned that $Au(OTeF_5)_3$ also contains bridging teflate groups in the solid state.[11]

Experimental Section

Reagents and Solvents. Toluene, benzene-d_6, and hexane were distilled from sodium. Dichloromethane, dichloromethane-d_2, and acetonitrile were distilled from CaH_2. These solvents were stored under vacuum or under a purified dinitrogen atmosphere prior to use. Silver(I) fluoride (Cerac) and AgCN (Aldrich) were used as received. Teflic acid,[12] $HOTeF_5$, was prepared by literature procedures.[13,14]

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 ^{19}F NMR spectroscopy were dichloromethane or toluene solutions with 1% $CFCl_3$ added. Chemical shifts (δ scale) are relative to the $CFCl_3$ internal standard. Spectra were recorded at room temperature on a Bruker SY-200 spectrometer operating at 188.31 MHz. All ^{19}F NMR spectra were AB_4X patterns upfield of $CFCl_3$ ($X = {}^{125}Te$, 7.0% natural abundance, $I = {}^1/_2$).

Samples for ^1H NMR spectroscopy were dichloromethane-d_2 or benzene-d_6 solutions with 1% Me_4Si added. Spectra were recorded 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, toluene, or acetonitrile, 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^{-1}.

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 molecular weight of $[AgOTeF_5(C_6H_5CH_3)_2]_2$ in toluene solution was measured with use of an isopiestic molecular-weight apparatus.[15] Tris(acetylacetonato)iron(III) (recrystallized from benzene) was used as the molecular weight standard.

Preparation of Compounds. $\mathbf{AgOTeF_5{\cdot}CH_2Cl_2}$. Anhydrous AgF (3.8 g, 30 mmol) and dichloromethane (30 mL) were charged into a stainless steel vessel equipped with a stainless steel valve and a Kel-F valve seat. Teflic acid (6.7 g, 28 mmol) was vacuum transferred into the reaction vessel at −196 °C. The reaction mixture was agitated for 3 h at room temperature. Removal of all volatiles under vacuum left a free-flowing gray powder. This was immediately dissolved in a minimum of dichloromethane and filtered, leaving a colorless solution. Flash evaporation of the solvent left a white powder, formulated (see below) as $AgOTeF_5{\cdot}CH_2Cl_2$ (>85% yield based on $HOTeF_5$). ^{19}F NMR (dichloromethane): δ_A −30.0, δ_B −41.2, $J_{AB} = 180$ Hz, $J_{AX} = 3041$ Hz, $J_{BX} = 3626$ Hz.

$\mathbf{[AgOTeF_5(C_6H_5CH_3)_2]_2}$. The above procedure was repeated with toluene in place of dichloromethane. A white powder, $[AgOTeF_5(C_6H_5CH_3)_2]_2$, can be isolated in 10-g batches (>90% yield based on $HOTeF_5$). Crystals suitable for diffraction were grown by slowly cooling a saturated toluene solution of this compound. ^{19}F NMR (toluene): δ_A −26.1, δ_B −37.9, $J_{AB} = 180$ Hz, $J_{AX} = 3030$ Hz, $J_{BX} = 3659$ Hz.

Table I. Experimental Parameters for the X-ray Diffraction Study

mol formula	$[AgOTeF_5(C_6H_5CH_3)_2]_2$
mol wt	1061.49 g/mol
space group	$P2_1/c$
unit cell dimens	
a	9.363 (2) Å
b	18.109 (4) Å
c	10.514 (2) Å
β	112.89 (2)°
unit cell volume	1642.3 Å^3
Z	2
calcd density	2.15 g cm^{-3}
cryst dimens	0.35 mm × 0.30 mm × 0.45 mm
data collecn temp	−130 °C
radiation	Mo Kα (λ = 0.71073 Å)
monochromator	graphite
abs coeff	30.38 cm^{-1}
2θ range	3.5–55°
unique reflcns	3798 for $h > 0$, $k > 0$, $\pm l$
obsd reflcns	3242 with $I > 2.5\sigma(I)$
scan type	θ–2θ
scan speed	variable, 2–30° min^{-1}
data/parameter ratio	15.8
R	0.027
R_w	0.030
GOF	1.44
g	4.3×10^{-4}
slope of normal probability plot	1.11

$\mathbf{[AgOTeF_5(CH_3CN)_2]_2}$. The preparation of this compound follows a literature procedure.[8,9] Silver(I) cyanide (1.1 g, 8.3 mmol) and acetonitrile (30 mL) were charged into a Schlenk flask. Very little of the AgCN dissolved. Teflic acid (2.0 g, 8.3 mmol) was vacuum transferred into the flask at −196 °C. The reaction mixture was stirred at room temperature for several hours, affording a colorless solution. Removal of all volatiles under vacuum left a sticky white solid.

Crystallographic Study. A colorless prism of $[AgOTeF_5(C_6H_5CH_3)_2]_2$ was centered on a Nicolet R3m diffractometer. The setting angles for 25 reflections ($2\theta(av) = 17.60°$) allowed least-squares calculation[16] of the cell constants. Relevant experimental parameters and results are listed in Table I.

The intensities of all reflections were measured by using θ–2θ scans, with a scan range of $[2.0 + 1.0(2\theta_{K\alpha_1} - 2\theta_{K\alpha_2})]°$, where the background measurement was taken for half the total scan time at the scan extremes. The intensities of control reflections (400, 060, 006) monitored every 97 reflections showed no significant trend during the course of the data collection.

An empirical absorption correction, based on intensity profiles for 15 reflections over a range of setting angles (ψ) for the diffraction vector, was applied to the observed data. The applied transmission factors ranged ±9% about the mean value. Lorentz and polarization corrections were carried out on the unique observed reflections used in the least-squares refinement. The space group was uniquely determined to be $P2_1/c$ (No. 14) by systematic absences for $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$).[17]

The tellurium and silver 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. Subsequent refinement involved anisotropic thermal parameters for all non-hydrogen atoms. Neutral-atom scattering factors (including anomalous scattering) were taken from ref 18. 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 <0.006 over the last six cycles.

In the final difference Fourier synthesis the maximum electron density was 0.99 e Å^{-3} in the immediate vicinity of the silver atom. The minimum electron density was 0.58 e Å^{-3}. Analysis of variance as a function

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(11) Seppelt, K., personal communication, 1984.

(12) We suggest the abbreviations teflate and teflic acid in place of the correct nomenclature pentafluoroorthotellurate and pentafluoroorthotelluric acid, respectively. The latter compound is the parent from which all teflates are prepared.[10]

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(16) Calculations involving diffractometer manipulations were performed with use of 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, using the SHELXTL program library written by Professor G. M. Sheldrick and supplied by Nicolet XRD Corp.

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Table II. Atomic Positional Parameters ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$)

atom	*x*	*y*	*z*	U^a
Ag	306 (1)	5756 (1)	3958 (1)	31 (1)
Te	1037 (1)	6112 (1)	7640 (1)	30 (1)
O	746 (3)	5450 (2)	6299 (3)	35 (1)
F(1)	981 (4)	5443 (2)	8948 (3)	51 (1)
F(2)	3173 (3)	6067 (2)	8377 (3)	56 (1)
F(3)	−1047 (3)	6303 (2)	7173 (3)	46 (1)
F(4)	1318 (4)	6807 (2)	9003 (3)	52 (1)
F(5)	1135 (3)	6917 (1)	6589 (2)	43 (1)
C(1)	2888 (5)	5372 (2)	4037 (5)	43 (2)
C(2)	3709 (5)	5830 (3)	5134 (5)	41 (2)
C(3)	4008 (4)	6562 (2)	4937 (4)	34 (1)
C(4)	3443 (5)	6832 (3)	3584 (5)	40 (2)
C(5)	2605 (5)	6388 (3)	2488 (5)	48 (2)
C(6)	2326 (5)	5659 (3)	2707 (5)	50 (2)
C(7)	4921 (7)	7050 (3)	6126 (5)	60 (2)
C(8)	−2507 (7)	6467 (3)	3672 (5)	64 (2)
C(9)	−3582 (6)	6028 (3)	2756 (6)	59 (2)
C(10)	−3594 (5)	5914 (3)	1455 (5)	49 (2)
C(11)	−2464 (6)	6252 (3)	1083 (5)	49 (2)
C(12)	−1399 (6)	6697 (3)	2083 (7)	59 (2)
C(13)	−1475 (6)	6805 (3)	3338 (5)	60 (2)
C(14)	−2437 (13)	6147 (5)	−322 (7)	120 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Bond Distances (Å) and Angles (deg) for $[AgOTeF_5(C_6H_5CH_3)_2]_2$

Ag–O	2.396 (3)	C(1)–C(2)	1.385 (6)
Ag–O′	2.368 (3)	C(2)–C(3)	1.387 (6)
Ag–C(1)	2.485 (5)	C(3)–C(4)	1.398 (6)
Ag–C(6)	2.697 (6)	C(4)–C(5)	1.373 (6)
Ag–C(12)	2.625 (5)	C(5)–C(6)	1.382 (8)
Ag–C(13)	2.443 (5)	C(3)–C(7)	1.498 (6)
Te–O	1.789 (3)	C(8)–C(13)	1.303 (10)
Te–F(1)	1.848 (3)	C(8)–C(9)	1.348 (7)
Te–F(2)	1.845 (3)	C(9)–C(10)	1.379 (9)
Te–F(3)	1.850 (3)	C(10)–C(11)	1.403 (8)
Te–F(4)	1.848 (3)	C(11)–C(12)	1.390 (7)
Te–F(5)	1.853 (3)	C(12)–C(13)	1.362 (10)
C(1)–C(6)	1.389 (7)	C(11)–C(14)	1.499 (11)
Ag–O–Ag′	101.4 (1)	C(1)–Ag–C(13)	141.3 (2)
O–Ag–O′	78.6 (1)	C(6)–Ag–C(12)	90.7 (2)
O–Ag–C(1)	97.2 (1)	C(6)–Ag–C(13)	117.1 (2)
O–Ag–C(6)	127.8 (1)	C(12)–Ag–C(13)	30.9 (2)
O–Ag–C(12)	137.1 (2)	Ag–C(1)–C(2)	94.5 (3)
O–Ag–C(13)	106.3 (2)	Ag–C(1)–C(6)	83.1 (3)
O′–Ag–C(1)	95.9 (1)	Ag–C(6)–C(1)	66.2 (3)
O′–Ag–C(6)	102.9 (1)	Ag–C(6)–C(5)	103.4 (4)
O′–Ag–C(12)	114.1 (1)	Ag–C(12)–C(11)	103.9 (3)
O′–Ag–C(13)	118.5 (1)	Ag–C(12)–C(13)	67.2 (3)
Ag–O–Te	124.6 (1)	Ag–C(13)–C(8)	93.6 (4)
Ag′–O–Te	129.5 (2)	Ag–C(13)–C(12)	81.9 (3)
O–Te–F(1)	96.2 (1)	C(1)–C(2)–C(3)	121.8 (4)
O–Te–F(2)	96.3 (1)	C(2)–C(3)–C(7)	121.4 (4)
O–Te–F(3)	95.4 (1)	C(2)–C(3)–C(4)	117.9 (4)
O–Te–F(4)	179.0 (1)	C(3)–C(4)–C(5)	121.0 (4)
O–Te–F(5)	94.8 (1)	C(4)–C(3)–C(7)	120.7 (4)
F(1)–Te–F(2)	89.9 (1)	C(4)–C(5)–C(6)	120.2 (4)
F(1)–Te–F(3)	89.3 (1)	C(5)–C(6)–C(1)	120.1 (4)
F(1)–Te–F(4)	84.6 (1)	C(6)–C(1)–C(2)	119.0 (4)
F(1)–Te–F(5)	168.9 (1)	C(8)–C(9)–C(10)	120.8 (6)
F(2)–Te–F(3)	168.3 (1)	C(9)–C(10)–C(11)	119.7 (4)
F(2)–Te–F(4)	84.2 (1)	C(10)–C(11)–C(14)	121.5 (5)
F(2)–Te–F(5)	89.3 (1)	C(10)–C(11)–C(12)	116.0 (5)
F(3)–Te–F(4)	84.0 (1)	C(11)–C(12)–C(13)	121.6 (6)
F(3)–Te–F(5)	89.2 (1)	C(12)–C(11)–C(14)	122.4 (7)
F(4)–Te–F(5)	84.3 (1)	C(12)–C(13)–C(8)	121.1 (5)
C(1)–Ag–C(6)	30.8 (2)	C(13)–C(8)–C(9)	120.7 (6)
C(1)–Ag–C(12)	120.4 (2)		

of Bragg angle, magnitude of F_0, reflection indices, etc., showed no significant trends.

Table II contains a list of atomic positional parameters and equivalent isotropic thermal parameters. Table III contains a list of bond distances and angles. Also available as supplementary material are lists of hydrogen atom positions and isotropic thermal parameters (Table S1), anisotropic thermal parameters for non-hydrogen atoms (Table S2), and observed and calculated structure factors (Table S3). See paragraph at the end of the paper regarding supplementary material.

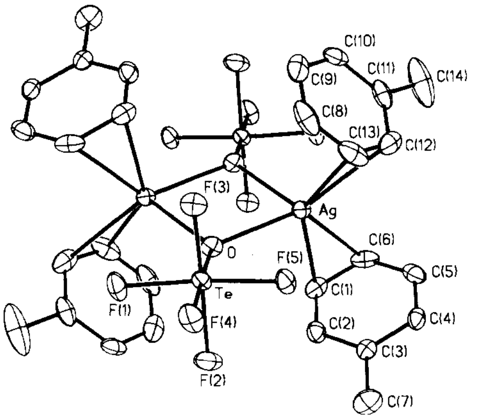

Figure 1. ORTEP drawing of the centrosymmetric molecule $[AgOTeF_5(C_6H_5CH_3)_2]_2$ (50% probability ellipsoids, hydrogen atoms omitted).

Results and Discussion

Preparation of Compounds. The reaction of solid AgF and a dichloromethane solution of the strong acid[14,19-21] $HOTeF_5$ proceeds rapidly at room temperature (eq 1). The purified white

$$AgF + HOTeF_5 \xrightarrow[\text{room temp, 3 h}]{CH_2Cl_2} \xrightarrow[-HF]{\text{vacuum}} AgOTeF_5{\cdot}CH_2Cl_2 \quad (1)$$

powder is freely soluble in dichloromethane (solutions exceeding 1 M have been prepared) and toluene, forming colorless solutions. Crystals that rapidly effloresce in a dinitrogen atmosphere can be grown, with much difficulty, from a cold (−78 °C) dichloromethane solution. Even after prolonged vacuum drying at room temperature, the purified white powder still contains 1.05 (8) equiv of dichloromethane/equivalent of $AgOTeF_5$. This was quantified (duplicate samples from two separate preparations) by preparing a solution of the powder of known concentration in benzene-d_6 and integrating the observed dichloromethane resonance vs. the standardized C_6D_5H resonance. On this basis the product is formulated as $AgOTeF_5{\cdot}CH_2Cl_2$. When the compound is stored at room temperature under ambient light for several days, approximately 10% of it is converted to insoluble, as yet uncharacterized, products (this photochemical and/or thermal instability has so far precluded an accurate elemental analysis). Nevertheless, $AgOTeF_5{\cdot}CH_2Cl_2$ can be easily used as a halide/teflate metathesis reagent[1g,h,3] if it is prepared, purified, and used within a few hours or if the purified white powder is stored at −78 °C in the dark.

Facile recrystallization of $AgOTeF_5{\cdot}CH_2Cl_2$ from toluene yields $[AgOTeF_5(C_6H_5CH_3)_2]_2$, the dimeric structure of which is shown in Figure 1 and discussed below. This compound can also be prepared directly from AgF and $HOTeF_5$ in toluene solution. The colorless crystals are thermally stable indefinitely in a dinitrogen atmosphere at −15 °C in the dark. Isopiestic measurements (toluene solution, duplicate samples) show that the apparent molecular weight of this compound is 1160 ± 100; the weight calculated for $[AgOTeF_5(C_6H_5CH_3)_2]_2$ is 1062. Thus, the bis(toluene) adduct of $AgOTeF_5$ is dimeric in toluene solution as well as in the solid state.

The reaction of AgCN and $HOTeF_5$ in acetonitrile solution yields HCN and a white pasty material. This reaction was reported earlier by Sladky and co-workers, who formulated the white product as $AgOTeF_5(CH_3CN)_x$.[5] We have found that AgCN does not react with neat $HOTeF_5$ (50 °C) or with $HOTeF_5$ in dichloromethane solution. We have also found that Sladky's product

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(21) We have found that $HOTeF_5$ will completely protonate chloride ion in dichloromethane solution.[14]

Table IV. Comparison of Relevant Bond Distances (Å) and Angles (deg)[a]

dist or angle	$[AgOTeF_5(C_6H_5CH_3)_2]_2$	$[AgClO_4(o\text{-xyl})_2]_2$[b]
Ag–C(*X*)	*X* = 1, 2.485 (5)	*X* = 1, 2.49 (3)
	X = 6, 2.697 (6)	*X* = 6, 2.57 (3)
	X = 12, 2.625 (5)	*X* = 7, 2.44 (3)
	X = 13, 2.443 (5)	*X* = 12, 2.53 (3)
Ag–O	2.368 (3), 2.396 (3)	2.56 (3), 2.60 (3)
Ag–O–Ag	78.6 (1)	71 (1)
O–Ag–O	101.4 (1)	109 (1)

[a] Both compounds are centrosymmetric dimers with Ag_2O_2 cores. [b] Reference 22; *o*-xyl = *o*-xylene.

Table V. Spectral and Structural Data for Representative $OTeF_5$ Compounds

compd	ν(TeO),[a] cm^{-1}	Te–O dist, Å	δ_A[b]
$B(OTeF_5)_3$	<740[c]	1.874 (6)[d]	−46.2[e]
$[N(n\text{-}Bu)_4]^+[B(OTeF_5)_4]^-$	795		−38.3[e]
$[Au(OTeF_5)_3]_2$	812[f,g]	1.91 (2)[g]	
$Pt(OTeF_5)_2(NBD)$	818[h,i]		−32.8[h]
$[N(n\text{-}Bu)_4]^+[H(OTeF_5)_2]^-$	814[j,k]	1.798 (4), 1.802 (4)[k]	−32.0[k]
$[AgOTeF_5(C_6H_5CH_3)_2]_2$	827[l,m]	1.789 (3)[m]	−29.9[m]
$Mn(CO)_5(OTeF_5)$	848[n]	1.75 (1)[n]	−30.8[n]
$[N(n\text{-}Bu)_4]^+[OTeF_5]^-$	867[k]		−19.0[k]

[a] Solid-state IR data unless otherwise noted. [b] ^{19}F NMR chemical shift (dichloromethane, 22 °C, $CFCl_3$ internal standard) of fluorine trans to oxygen. [c] Highest energy band attributable to ν(TeO) or ν(TeF). See ref 34. [d] Reference 35. [e] Strauss, S. H.; Abney, K. D., unpublished data. [f] From Raman spectrum of the solid. [g] Reference 30. [h] Reference 3; NBD = norbornadiene. [i] Average of two observed IR bands (808 and 827 cm^{-1}). [j] Average of two observed IR bands (861 and 766 cm^{-1}). [k] Reference 14. [l] Average of IR (819 cm^{-1}) and Raman (836 cm^{-1}) bands from spectra of the solid. [m] This work. [n] Reference 2.

probably contains bridging teflate groups and is best formulated as $[AgOTeF_5(CH_3CN)_2]_2$ (see below).

Structure of $[AgOTeF_5(C_6H_5CH_3)_2]_2$. A view of the centrosymmetric dimeric molecule is shown in Figure 1. The coordination sphere around each silver atom is pseudotetrahedral, being made up of two oxygen atoms from two bridging teflate groups and two carbon–carbon π bonds from two different η^2-toluene molecules; an ortho–meta bond in one toluene molecule and a meta–para bond in the other. A large number of silver(I)–arene complexes have been structurally investigated.[22-25] In all of these structures, the arenes are always found to be η^2 coordinated to the silver ions; η^4 or η^6 coordination is never observed. Most of the compounds studied contain perchlorate ions coordinated in a variety of ways to the silver ions.[22-24] A subset of these have the empirical formula $AgClO_4(arene)_2$,[22,23] and one of these, $[AgClO_4(o\text{-xyl})_2]_2$[22] (*o*-xyl = *o*-xylene), consists of discrete dimers that are structurally similar to $[AgOTeF_5(C_6H_5CH_3)_2]_2$ and hence warrants a detailed comparison with our compound.

Both compounds contain μ,η^1 anions forming planar Ag_2O_2 cores. In the compound $[AgClO_4(o\text{-xyl})_2]_2$, each silver(I) ion is also coordinated to two carbon–carbon π bonds from two different η^2-arene molecules: a meta(C(1))–meta(C(6)) bond in one *o*-xylene molecule and an ortho(C(7))–meta(C(12)) bond in the other. A list of relevant distances and angles for both compounds is presented in Table IV.

The asymmetry in the Ag–C bonding to each arene in both compounds is easily seen. This is normal for silver(I)–arene complexes and has been adequately discussed in the literature.[23] To summarize, we focus on the Ag–C(1)–C(6) triangle in our compound. Instead of symmetric η^2-bonding, the Ag–C(1) distance of 2.485 (5) Å is significantly shorter than the Ag–C(6)-distance of 2.697 (6) Å. The angles at Ag, C(6), and C(1) of 30.8 (2), 66.2 (3), and 83.1 (3)°, respectively, nearly describe a 30–60–90° right triangle perpendicular to the plane of the toluene molecule (note that the Ag–C(1)–C(2) angle is 94.5 (3)°). Thus, the silver ion is close to sitting on a line through C(1) and normal to the toluene molecule. One can argue that the bonding is better described as η^1 instead of η^2. In any event, this type of asymmetry has been used to argue that silver(I)–arene bonding is predominantly arene-to-silver(I) σ donation with little silver(I)-to-arene π back-bonding.[23]

The most significant feature of this structure is the observation that the $OTeF_5$ group can bridge two elements. Despite the sizable literature on this pseudohalogen, bridge formation has not been observed or suggested.[10] While this work was in progress, we learned that $Au(OTeF_5)_3$ also contains bridging teflates in the solid state.[30] Despite a severe disorder, gold(III) teflate has been found to crystallize with the Au_2Cl_6 structure:[30,31] each gold atom of the dimeric molecule has a square-planar geometry with two terminal $OTeF_5$ groups and two bridging $OTeF_5$ groups shared with the other gold atom. The two gold and six oxygen atoms are nearly coplanar.[30] The Au–O(bridge) distances of 2.23 (4) and 2.29 (4) Å are significantly shorter than the Ag–O distances in our compound.[32] This probably reflects the smaller radius of Au(III) vs. that of Ag(I) and an expected greater covalent character for gold(III)–oxygen vs. silver(I)–oxygen bonds. These two structures demonstrate that teflate is electronically and sterically capable of serving as a bridging ligand in some cases.

Despite the expectation that bridging teflates should be sterically more demanding than η^1-bridging perchlorates, the Ag–O distances of 2.368 (3) and 2.396 (3) Å in our compound are much shorter than the Ag–O distances of 2.56 (3) and 2.60 (3) Å in $[AgClO_4(o\text{-xyl})_2]_2$. This observation, coupled with other data that we have reported[2] or are accumulating,[1g,h,3] lead to the conclusion that teflate is a stronger ligand and is electronically quite different from other monovalent oxygen-containing anions such as perchlorate or triflate ($CF_3SO_3^-$).[26,27] Since the sum of covalent and ionic radii for silver(I) and oxygen are 2.18[28] and 2.66 Å,[29] respectively, the silver(I)–oxygen bonds in $[AgOTeF_5(C_6H_5CH_3)_2]_2$ probably have a sizable amount of ionic character. This is confirmed by spectroscopic data, given below.

Spectroscopic Measurements. Spectral and structural data for a main-group and transition-metal teflate compounds show that a correlation exists between the tellurium–oxygen stretching frequency (ν(TeO)), the ^{19}F NMR chemical shift of the fluorine atom trans to oxygen (δ_A),[33] and the Te–O distance. Data for a representative set of compounds are collected in Table V.[34,35]

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(26) See ref 2 for a list of structurally characterized $OTeF_5$ compounds.

(27) As an example, the electronic spectra of $Mn(CO)_5X$ complexes[2] show that teflate behaves electronically more like iodide than like chloride, perchlorate, or triflate (the lowest energy band in the electronic spectrum of $Mn(CO)_5(CF_3SO_3)$ is centered at 380 nm in dichloromethane: Trogler, W. C., personal communication).

(28) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 246.

(29) Reference 28, p 514.

(30) Huppmann, P.; Hartl, H.; Seppelt, K., submitted for publication in *Z. Anorg. Allg. Chem.*

(31) Wells, A. F. "Structural Inorganic Chemistry", 5th ed.; Oxford University Press: Oxford, England, 1984; p 1147.

(32) The Au–O(terminal) distances are 1.78 (4) and 1.82 (3) Å; for the Au_2O_2 core the angle at gold is 75 (1)° while the angle at the bridging oxygen is 101 (2)°.[30]

(33) Fluorine-19 chemical shifts for a variety of main-group teflate compounds can be found in: Seppelt, K. *Z. Anorg. Allg. Chem.* **1973**, *399*, 65.

(34) Kropshofer, H.; Leitzke, O.; Peringer, P.; Sladky, F. *Chem. Ber.* **1981**, *114*, 2644.

Table VI. Te–O Stretching Frequencies (cm^{-1})

compd	medium	ν(TeO), cm^{-1} ($\Delta\nu_{1/2}$, cm^{-1}) IR	Raman
$[AgOTeF_5(C_6H_5CH_3)_2]_2$	solid state	819 (17)	836 (7)
	toluene	819 (10)	
$[AgOTeF_5(CH_3CN)_2]_2$	solid state	832 (50)[a]	842 (7)
	acetonitrile	850 (16), 861 (11)[b]	
$AgOTeF_5{\cdot}CH_2Cl_2$	solid state	815 (25)	812 (11), 845 (7)
	dichloromethane	818 (9)	

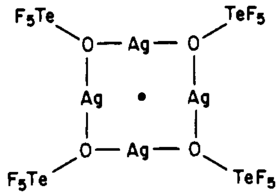
[a] ν(CN): 2312, 2285 cm^{-1}, equal intensity. [b] The relative intensities of these two bands were concentration dependent (see also ref 8). The band at 861 cm^{-1} is due to free $OTeF_5^-$.[14]

The free $OTeF_5^-$ anion has the maximum amount of O-to-Te p–d π bonding, resulting in the strongest (and presumably shortest[36]) Te–O bond with the highest ν(TeO) value. A normal-coordinate analysis[8] of $OTeF_5^-$ and vibrational data for other teflate derivatives[36] have shown that the tellurium–oxygen stretching force constant is larger for free $OTeF_5^-$ than for either ion-paired $OTeF_5^-$ or covalent teflates. The interaction of any other element with the teflate oxygen decreases the O-to-Te p–d π bonding, progressively weakening and lengthening the tellurium–oxygen bond. The extreme situation is found in $B(OTeF_5)_3$, with a Te–O distance of 1.874 (6) Å;[34] in this case O-to-B p–p π bonding severely limits the double-bond character of the tellurium–oxygen bond (the benchmark for a tellurium–oxygen single-bond distance is 1.91 Å, the average of the Te–O distances found in the monoclinic modification of $Te(OH)_6$[37]).

The correlations in Table V can be used qualitatively as follows: if ν(TeO) is greater than ~820 cm^{-1} and/or the Te–O distance is less than 1.80 Å, the teflate portion of the molecule (and hence the bond from the element in question to oxygen) has appreciable ionic character. Our compound fits these criteria. That the silver(I)–oxygen bonds are quite ionic is chemically reasonable, given the nature of silver(I) (soft) and the electronegative teflate oxygen (hard).

An important application of ν(TeO) data is the demonstration that $AgOTeF_5{\cdot}CH_2Cl_2$ and Sladky's $AgOTeF_5(CH_3CN)_x$ also contain bridging $OTeF_5$ groups in the solid state. Note that the Te–O oscillators in $[AgOTeF_5(C_6H_5CH_3)_2]_2$ are strongly coupled; the centrosymmetric compound has an IR band at 819 cm^{-1} and a Raman band at 836 cm^{-1}, which we ascribe to $\nu(TeO)_{asym}$ and $\nu(TeO)_{sym}$, respectively (Table VI). Two similar bands are also observed in the solid-state vibrational spectra of $AgOTeF_5(CH_3CN)_x$. We suggest that the solid compound is also a centrosymmetric dimer with bridging teflates and is best formulated as $[AgOTeF_5(CH_3CN)_2]_2$ (Table VI). Substitution of acetonitrile for toluene as a ligand should more effectively neutralize the charge on the metal, weaken the silver(I)–oxygen bonds, and hence strengthen the tellurium–oxygen bonds. Thus, it is reasonable that ν(TeO) bands for $[AgOTeF_5(CH_3CN)_2]_2$ are found at higher energy than for $[AgOTeF_5(C_6H_5CH_3)_2]_2$.

The compound $AgOTeF_5{\cdot}CH_2Cl_2$ exhibits one IR and two Raman bands in the ν(TeO) region (Table VI). One chemically reasonable structure for this compound that is compatible with these spectral results is



A D_{4h} Ag_4O_4 geometry would give rise to two ν(TeO) Raman bands and one doubly degenerate ν(TeO) IR band and is not without structural precedent: the compound KAgO contains discrete, planar $Ag_4O_4^{4-}$ anion tetramers.[38] Attempts to study this interesting, but photochemically/thermally unstable, compound by X-ray diffraction and molecular weight measurements are continuing.

Conclusions. The new compounds $AgOTeF_5{\cdot}CH_2Cl_2$ and $[AgOTeF_5(C_6H_5CH_3)_2]_2$, which have been found to be excellent teflate/halide metathesis reagents,[1g,h,3] have been prepared. The solid-state structure of the latter compound is unusual in that it is a dimer containing bridging teflates. A molecular weight determination demonstrates that the compound is also dimeric in toluene solution. We infer from this result that the solid-state structure is retained in solution. Spectroscopic data show that the two Te–O bonds are vibrationally coupled across the Ag_2O_2 core. This result is important in that it suggests a straightforward and simple way to detect bridging teflates in compounds with $M_2(OTeF_5)_2$ cores, more of which will probably be discovered as more transition-metal teflate chemistry is explored. We have used the noncoincidence of IR and Raman ν(Te–O) bands to argue that $AgOTeF_5{\cdot}CH_2Cl_2$ and $AgOTeF_5(CH_3CN)_x$ also contain bridging teflate groups in the solid state. The latter compound was originally prepared by Sladky et al. and has been reformulated by us as $[AgOTeF_5(CH_3CN)_2]_2$.

The structure of $[AgOTeF_5(C_6H_5CH_3)_2]_2$ has additional significance in that a comparison of the coordinating ability of $OTeF_5^-$ and ClO_4^- can be made for the first time. Both monovalent oxoanions are derived from strong acids and contain a central atom in its highest oxidation state. However, the Ag–O bond distances in our compound are significantly shorter than those in the structurally similar compound $[AgClO_4(o\text{-xyl})_2]_2$. Since the steric requirements for $OTeF_5^-$ are probably greater than for ClO_4^-, our structure demonstrates that teflate is a much stronger ligand than perchlorate.

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Registry No. $AgOTeF_5$, 50700-88-4; $[AgOTeF_5(C_6H_5CH_3)_2]_2$, 98330-69-9; $[AgOTeF_5(CH_3CN)_2]_2$, 98330-70-2.

Supplementary Material Available: Listings of hydrogen atom positions and isotropic thermal parameters (Table S1), anisotropic thermal parameters for non-hydrogen atoms (Table S2), and observed and calculated structure factors (Table S3) (22 pages). Ordering information is given on any current masthead page.

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(36) The Te–O distance in free $OTeF_5^-$ is not known, since salts such as $Cs^+OTeF_5^-$ are at least threefold disordered in the solid state.[9]

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